

Kinetics and Selectivity of Deep
Catalytic Oxidation of Volatile
Organic Compound Mixtures

Research Triangle Inst.
Research Triangle Park, NC

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Jan 87



KINETICS AND SELECTIVITY OF DEEP CATALYTIC OXIDATION
OF VOLATILE ORGANIC COMPOUND MIXTURES

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CR812522

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U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)			
1. REPORT NO. EPA/600/D-87/045		3. RECIPIENT'S ACCESSION NO. PB87 147179/AS	
4. TITLE AND SUBTITLE Kinetics and Selectivity of Deep Catalytic Oxidation of Volatile Organic Compound Mixtures		5. REPORT DATE January 1987	
7. AUTHOR(S) S. K. Gangwal, M. E. Mullins, J. J. Spivey, and P. R. Caffrey (RTI); and B. A. Tichenor (EPA)		6. PERFORMING ORGANIZATION CODE	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Research Triangle Institute P. O. Box 12194 Research Triangle Park, North Carolina 27709		8. PERFORMING ORGANIZATION REPORT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711		10. PROGRAM ELEMENT NO.	
		11. CONTRACT/GRANT NO. CR812522	
		13. TYPE OF REPORT AND PERIOD COVERED Paper; October 1986	
		14. SPONSORING AGENCY CODE EPA/600/13	
15. SUPPLEMENTARY NOTES AEERL project officer is Bruce A. Tichenor, Mail Drop 54, 919/541-2991. Presented at AIChE meeting, Miami Beach, FL, 11/2-7/86.			
16. ABSTRACT The paper gives results of a fundamental study of low-temperature deep (complete) oxidation of n-hexane, benzene, and ethyl acetate over a 0.1% Pt, 3% Ni/gamma-AL2O3 catalyst. (NOTE: Deep catalytic combustion of volatile organic compounds--VOCs--is emerging as an important emission control technique.) These VOCs were subjected to oxidation as single components and as binary and ternary mixtures at temperatures of 160-360 C. n-Hexane oxidation was significantly inhibited in the mixtures, and ethyl acetate oxidation was significantly enhanced in the mixtures. An approach based on the Mars/van Krevlan rate model is being used to explain these inhibitions and enhancements. Kinetic parameters were developed for the individual VOCs based on single component differential reactor data. These kinetic parameters were incorporated into a proposed multicomponent Mars/van Krevlan rate model to predict the experimental conversions in multicomponent mixtures. The model was reasonable successful in predicting the conversion of benzene and n-hexane in their binary mixture, in the intrinsic kinetic region. However, as expected, it overpredicted the conversions in the mass transfer region, since the effect of mass transfer was not incorporated. The model was unsuccessful in predicting conversions for all species in mixtures containing ethyl acetate.			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Selectivity	Pollution Control	13B 14G
Organic Compounds	Benzene	Stationary Sources	07C
Volatility	Ethyl Acetate	Volatile Organic Compounds	20M
Oxidation	Hexanes	Catalytic Oxidation	07B
Catalysis			07D
Kinetics			20K
18. DISTRIBUTION STATEMENT Release to Public		19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 49
		20. SECURITY CLASS (This page) Unclassified	22. PRICE

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ABSTRACT

Deep (complete) catalytic combustion (oxidation) of volatile organic compounds (VOCs) is emerging as an important emission control technique. A fundamental study was carried out for low-temperature deep oxidation of n-hexane, benzene, and ethyl acetate over a 0.1-percent Pt, 3-percent Ni/ γ -Al₂O₃ catalyst. These VOCs were subjected to oxidation as single components and as binary and ternary mixtures at temperatures ranging from 160 to 360 °C. n-Hexane oxidation was significantly inhibited in the mixtures, and ethyl acetate oxidation was significantly enhanced in the mixtures. An approach based on the Mars/van Krevlan rate model is being used to explain these inhibitions and enhancements. Kinetic parameters were developed for the individual VOCs based on single component differential reactor data. These kinetic parameters were then incorporated into a proposed multicomponent Mars/van Krevlan rate model to predict the experimental conversions in multicomponent mixtures. The model was reasonably successful in predicting the conversion of benzene and n-hexane in their binary mixture, in the intrinsic kinetic region. However, as expected, it overpredicted the conversions in the mass transfer region, since the effect of mass transfer was not incorporated. The model was unsuccessful in predicting conversions for all species in mixtures containing ethyl acetate. The enhancement of ethyl acetate oxidation in mixtures may be due to second order interactions (cocatalysis) between other hydrocarbon species and ethyl acetate.

INTRODUCTION

The subject of heterogeneous catalytic oxidation of organic compounds in the vapor phase has been reviewed by various authors (Prasad et al. 1984, Golodets 1983, Butt 1976, Margolis 1973, Germain 1969, Cullis 1967, Dixon and Longfield 1960). From an industrial perspective, two different types of heterogeneous catalytic oxidation processes may be recognized: (1) partial oxidation for manufacturing of commercially significant products (e.g., ethylene to ethylene oxide, benzene to maleic anhydride, and naphthalene to phthalic anhydride) and (2) deep (or complete) oxidation of trace (low concentration) organic contaminants in air (e.g., for air purification, industrial emission control, and automotive exhaust catalysis). The low-temperature, deep oxidation of trace organic contaminants, referred to as volatile organic compounds (VOCs) herein, is the subject of this paper. Deep oxidation is carried out using highly active, nonselective catalysts containing either noble metals (Pt, Pd, Rh), oxides of base metals (Co, Ni, Mn), or various combinations of these materials. The temperature range of primary interest to this study is 160 to 360 °C.

Reported applications for deep oxidation include odor removal from sewage pumping off-gases (Bonacci and Heck 1983), polymer-processing vapor control (Budd 1978), odor control from coffee-roasting gases (Balough et al. 1975), and solvent emission abatement in automotive spray painting (Roberts and Roberts 1976). Because the compositions of the gas streams containing the oxidizable compounds were very complex, the overall performances of these field systems are reported in terms of gross parameters, such as "odor reduction" or "percent carbon removal," and do not allow evaluation of the effect of the presence of any one compound in the oxidizable mixture on the oxidation of other compounds. On the other hand, reported fundamental research studies are generally for single compounds only (Golodets 1983).

Thus, there is a dearth of fundamental work in the reported literature focusing on deep catalytic oxidation of a mixture of VOCs. In general, catalyst selection for purification of air containing a mixture of VOCs is

based on determination of catalyst activity for single compounds in the input air (Christian and Johnson 1965, Johns 1966, Miller and Piatt 1960, Rousseau 1964). However, as pointed out by Musick et al. (1972), such determinations cannot be expected to show the possible effects of the simultaneous presence of a multitude of compounds. The fundamental investigation of these "mixture effects" is of primary interest in this paper.

This study was carried out under a Cooperative Agreement between the U.S. Environmental Protection Agency (EPA) and the Research Triangle Institute (RTI) with funding support from the U.S. Air Force via an Interagency Agreement with EPA. Over the past years, EPA has sponsored research to investigate the effectiveness of deep catalytic oxidation over a range of operating conditions and emission-stream characteristics (Martin 1981, Jennings et al. 1984). These initial studies emphasized the catalytic oxidation of total VOCs, rather than individual VOCs in the mixtures. In a more recent EPA-sponsored study (Palazzolo et al. 1985, Tichenor and Palazzolo 1985), the emphasis was on oxidation of the individual VOCs in the mixtures being oxidized. A pilot-scale catalytic incinerator (platinum/palladium catalyst on a ceramic honeycomb substrate) was operated at temperatures ranging from 260 to 425 °C and space velocities ranging from 15,000 to 80,000 h⁻¹. Eight multicomponent VOC mixtures with between two and seven VOCs in each mixture were tested. In addition, 16 of the VOCs were tested singly. These tests showed that a compound may behave quite differently when oxidized in a mixture versus when oxidized as a single compound. For example, n-hexane oxidation was found to be inhibited in mixtures, whereas ethyl acetate oxidation was found to be enhanced in mixtures.

Other past studies of the oxidation of a compound by itself and in a mixture generally show that mixtures inhibit the oxidation of the compound of interest, with few exceptions. Yao and Kummer (1973) studied the oxidation of C₂H₄, C₃H₆, C₂H₆, C₃H₈, and CO over NiO crystals. The olefins were retarded much less than the alkanes. The authors have attempted to explain their results by competition among the hydrocarbons for adsorbed O₂ or for undefined adsorption sites. Cullis et al. (1970) studied the oxidation of methane over a Pd/Al₂O₃ catalyst in the presence of propane, methanol,

formaldehyde, and dichloromethane. All these compounds retarded methane oxidation. Propane was oxidized very little compared to formaldehyde and methanol. Dichloromethane inhibited deep oxidation but enhanced partial oxidation of methane to formaldehyde. Musick et al. (1972) carried out oxidation experiments involving CO, H₂, CH₄, C₃H₈, benzene, thiophene, and monochlorodifluoromethane over a Cu-Mn oxide catalyst (hopcalite), a supported hopcalite containing 0.02 percent Pd, and a supported Pt catalyst (0.5 percent Pt on Al₂O₃) in the presence of humidified air at 315 °C and 21,000 h⁻¹ space velocity. This study evaluated either CO by itself or CO mixed with one or more of the other compounds. Benzene inhibited CO oxidation, whereas thiophene partially poisoned the catalysts in addition to inhibiting CO oxidation. The poisoning of the catalyst and inhibition of CO oxidation due to thiophene appeared to proceed as independent phenomena, as evidenced by the partial recovery of catalyst activity when thiophene was taken off stream. The catalytic activity for CO oxidation was inhibited by all compounds except methane on the hopcalite catalyst and was uninhibited by all compounds except H₂ on the Pt catalyst. Interestingly, methane slightly enhanced CO oxidation on the hopcalite catalyst.

In addition to purely kinetic effects at low to moderate temperatures, the interpretation of data on mixture effects may be further complicated due to mass transfer effects at higher temperatures. The Cooperative Agreement between EPA and RTI has been established to gain a fundamental understanding of mixture effects in deep catalytic oxidation of VOCs. The approach that has been taken involves systematic evaluation of deep catalytic oxidation of VOC mixtures containing organic compounds of different classes of commercial catalysts. This paper presents some initial results of this ongoing study of oxidation of mixtures containing n-hexane, benzene, and ethyl acetate over a commercial 0.1-percent Pt, 3-percent Ni/ γ -Al₂O₃ catalyst.

EXPERIMENTAL

Chemicals

Benzene, n-hexane, and ethyl acetate premixed with hydrocarbon free, dry air in gas cylinders at concentrations ranging from 10 to 600 ppmv hydrocarbon were obtained from Scott Specialty Gases, Plumsteadville, PA. A number of gases containing single components, binary mixtures, and ternary mixtures were obtained as shown in Table 1. The gases were used one at a time in the deep-oxidation experiments.

Catalysts

The catalyst was obtained from United Catalyst, Inc., Louisville, KY, as 1/4-in. (6.35 mm) cylinders. The commercial designation of the catalyst was G-43, and its nominal composition as supplied by the vendor was 0.1 percent Pt, 3 percent Ni/ γ -Al₂O₃. The catalyst was crushed and screened to two different particle sizes (120 x 170 and 60 x 80 mesh) prior to use in the oxidation experiments. The physical properties of the catalyst, as specified by the vendor and as measured in RTI's laboratory, are given in Table 2.

Apparatus

A laboratory-scale microreactor system, shown in Figure 1, was used for all the experiments. The premixed gas was delivered using a two-stage pressure regulator with the gas-flow split into two equal flows using two differential flow controllers as shown. One flow stream was passed through the microreactor, whereas the other was passed through a bypass line. The reactor consisted of a 60-cm-long Pyrex tube (6 mm O.D., 4 mm I.D. for the 60 x 80 mesh catalyst; 3 mm O.D., 1.5 mm I.D. for the 120 x 170 mesh catalyst), and the catalyst was positioned at the center of the tube using fine Pyrex wool plugs. The tube was surrounded by a three-zone 45-cm-long split tube furnace. The end zones were each 7.5-cm-long and the central zone was 30-cm-long. The temperature of each heating zone was controlled separately using proportional temperature controllers. Four 0.5-mm O.D. measurement thermocouples (type K) were mounted, equally spaced, along the small catalyst bed to ensure temperature uniformity. The temperature control was

TABLE 1. TEST GAS MIXTURES

	<u>Concentration in Air (ppmv)</u>
Single Hydrocarbon	benzene: 9, 69, 163, 375, 525 ethyl acetate: 53, 109, 238, 450 n-hexane: 201, 410, 566
Binary Mixtures	193 ppm benzene + 172 ppm ethyl acetate 189 ppm benzene + 190 ppm n-hexane 184 ppm ethyl acetate + 190 ppm n-hexane
Ternary Mixture	143 ppm benzene + 174 ppm ethyl acetate + 90 ppm n-hexane

TABLE 2. CATALYST CHARACTERISTICS

Vendor	Measured
Composition: 0.1% Pt, 3% Ni/ γ -Al ₂ O ₃	3.18% Ni, 48.2% Al, 46.3% oxygen
Form: 1/4-in. (6.35 mm) extrudates (crushed to 120 x 170 mesh and 60 x 80 mesh prior to use)	
BET Surface Area: 212 m ² /g	161 m ² /g
Pore Volume:	
0-150 nm (Nitrogen BET Method)	0.364 cm ³ /g
1.4 to 14 nm (CCl ₄ Method): 0.26 cm ³ /g	
1.4 to 80 nm (CCl ₄ Method): 0.28 cm ³ /g	
Mean Pore Radius (estimated)	3.6 nm
Particle Density	1.46 g/cm ³
Pore Volume Distribution (Mercury Porosimetry, 60,000 psi [414 MPa]):	
175 to 12 μ m	0.0 cm ³ /g
12 μ m to 80 nm	0.08 cm ³ /g
80 to 14 nm	0.01 cm ³ /g
14 to 2.9 nm	0.23 cm ³ /g

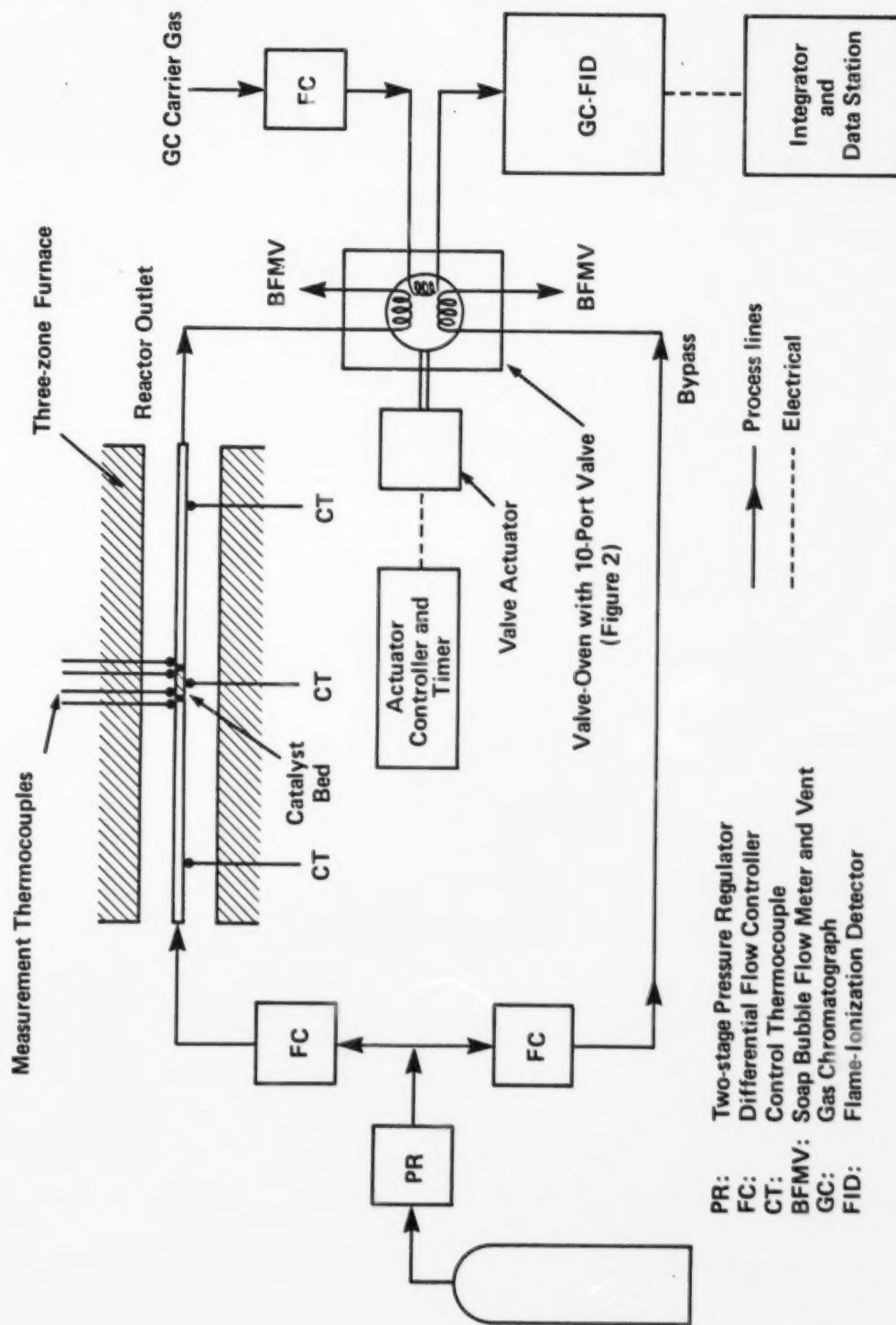


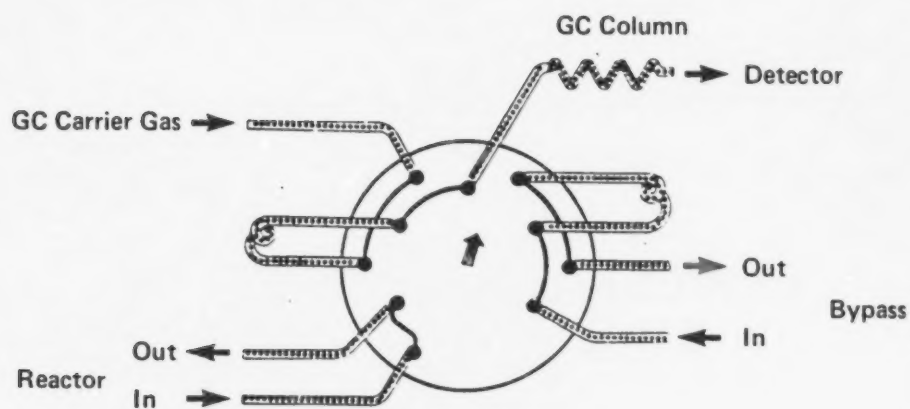
Figure 1. Microreactor system.

better than $\pm 0.5^{\circ}\text{C}$ in each zone. After the two split gas streams flowed through the reactor and the bypass line, they entered a thermostated Valco 10-port gas sampling valve maintained at 100°C . The 10-port valve is a unique device that allows sequential sampling of the reactor outlet stream and the bypass stream (i.e., representative of the reactor inlet stream) using two identical 0.25-cm^3 sample loops.

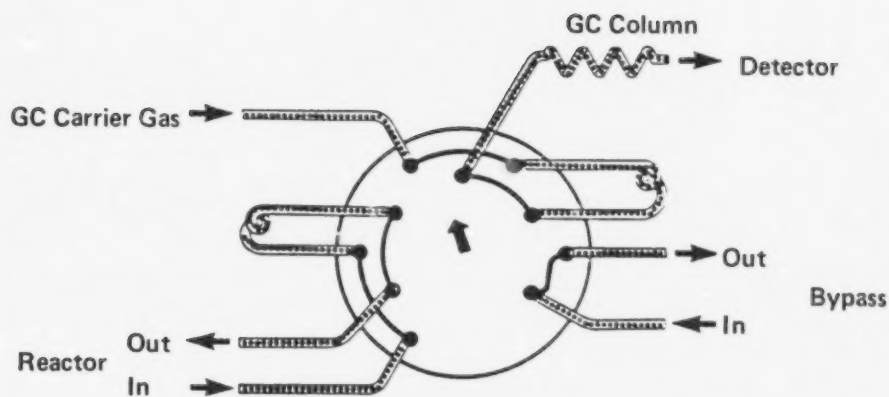
Sequential sampling using this valve is illustrated in Figure 2. The samples were injected automatically, using a Carle Valve Minder consisting of a valve actuator and a valve timer, into a Varian 3700 gas chromatograph equipped with a flame-ionization detector (FID). A 5 ft (1.5 m) long, 1/8-in. (3 mm) stainless-steel column consisting of 3 percent SP 1500 on 80/120 mesh Carbopack B was used for the separation and analysis of the hydrocarbons isothermally at 140°C . A complete analysis of the three hydrocarbons of interest could be performed in 4-1/2 minutes. The valve timer was placed on a 9-minute cycle to allow the measurement of the hydrocarbons in the reactor inlet and in the reactor outlet streams sequentially. Because the inlet concentration of the gas stream was a known constant, the outlet concentration was obtained assuming a linear response of the FID with respect to the inlet concentration for the hydrocarbons of interest. The analysis of the inlet during every cycle is extremely important because of variation of the FID response during the course of a typical day of the experiment. Even though the FID response may drift or cycle during the day, it would affect the outlet and the inlet stream concentrations in a fixed ratio. Thus, the sampling procedure allowed accurate measurement of the reactor outlet concentrations, irrespective of the drift in the FID response. The peak areas were measured electronically using a Perkin-Elmer Sigma 10B Data Station. The bypass and reactor outlet gas flows were measured using a soap bubble flow meter to ensure that they were equal. This equality of flow was necessary for accurate determination of the reactor outlet concentration.

Procedure

Typical experimental conditions (including reactor size, catalyst particle size, temperature range, pressure, and space velocities) are shown in



Valve Position A: Analyze reactor outlet



Valve Position B: Analyze reactor inlet (bypass)

Figure 2. Sequential analysis of reactor inlet (bypass) and reactor outlet gases with a 10-port "zero" volume valve.

Table 3. The experimental procedure consisted of measuring the reactor inlet and outlet concentrations at a series of constant temperatures and gas flow rates for each gas. Integral reactor high-conversion experiments were carried out initially. Single-component gases were run first, followed by the binary mixtures and the ternary mixture. These experiments allowed gross evaluations of the regimes of surface reaction, pore diffusion, external diffusion, and catalytically supported thermal reaction. These experiments also allowed us to establish whether or not mixture effects were present to a significant degree. More fundamental differential reactor experiments (less than 10 percent conversion) were then carried out for each pure component in the surface reaction controlled region to evaluate its rate expression. These rate expressions are used to explain the results of the integral reactor experiments and to evaluate mixture effects.

TABLE 3. EXPERIMENTAL CONDITIONS

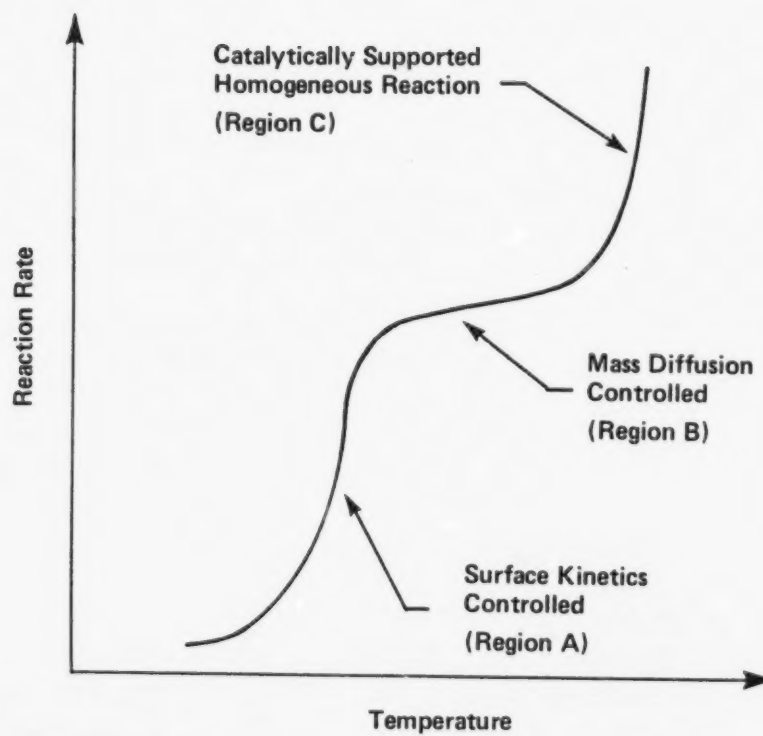
Pressure:	Atmospheric
Temperature Range:	140 to 360 °C (isothermal operation)
Space Velocity at Reaction Temperature:	50,000 to 1,000,000 h ⁻¹
Catalyst Bed:	17 to 20 mg
Hydrocarbon Concentration in Air:	10 to 600 ppmv
Catalyst Particle Size:	60 to 80 mesh, 120 to 170 mesh

RESULTS

During initial exposure of the 0.1-percent Pt, 3-percent Ni/ γ -Al₂O₃ catalyst to a hydrocarbon (VOC) containing air stream at approximately 300 °C, the catalyst exhibited a prolonged induction period (up to 72 hours) during which catalyst activity increased by nearly 2 orders of magnitude. Based on scanning electron microscopy/energy-dispersive x-ray analysis experiments, we believe that this induction period was caused primarily by slow redispersion of the Pt on the surface of the catalyst. Once the steady-state activity was reached, it remained stable throughout the duration of the experiments described herein. Only the steady-state results are presented in this paper. The induction period experiments and results will be discussed in a later paper.

Before presenting the results, it is instructive to consider the three operating regions of an industrial catalytic combustor as designated by Prasad et al. (1984) and shown in Figure 3. Generally, the inlet fuel/air mixture temperature is low, and the rate of combustion (oxidation) is controlled by intrinsic kinetics (region A). As temperature rises along the bed, the rate increases exponentially to a point where it is not possible to supply the reactant to the catalyst surface fast enough to keep up with the rate of reaction. This marks the beginning of the mass-transfer-controlled region (region B). The rate in region B may be controlled by external diffusion, internal (pore) diffusion, or a combination of both, depending on hydrodynamic conditions and catalyst physical structure. Farther downstream in the bed, the exothermic oxidation reactions increase the temperature to a point where gas-phase reactions begin to occur simultaneously with the catalytic reactions as the reaction completes. This region is designated as the catalytically supported homogeneous reaction region (region C), where the rate again increases exponentially.

Figures 4 through 6 show the conversion data for n-hexane, benzene, and ethyl acetate as a function of temperature in various mixtures. All these results were obtained at an identical weight hourly space velocity (WHSV) of 209, where WHSV is defined as the weight of the flowing gas per unit



Source: Prasad et al. (1984)

Figure 3. Rate controlling regimes in a catalytic combustor.
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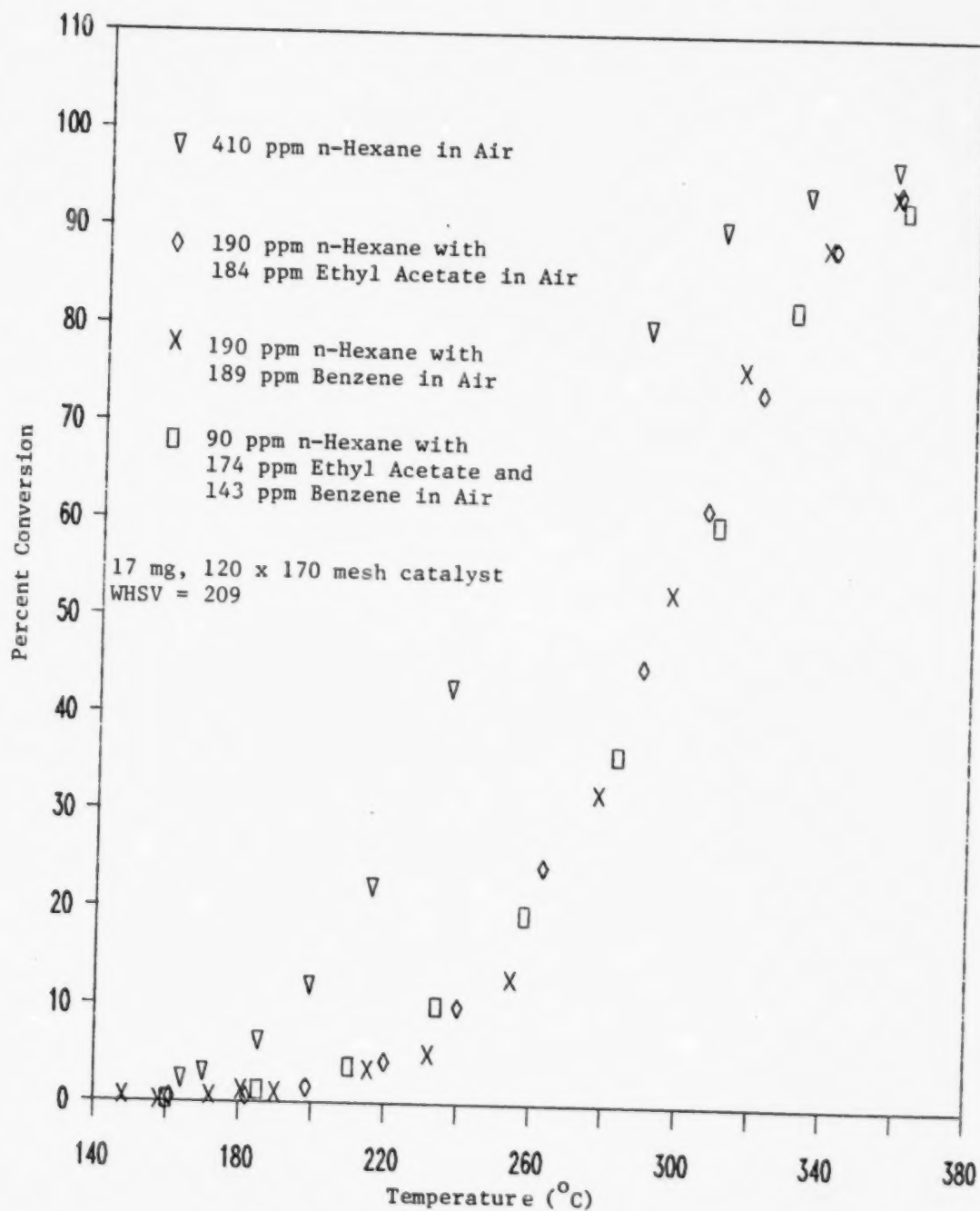


Figure 4. Effect of multicomponent mixtures on n-hexane conversion.

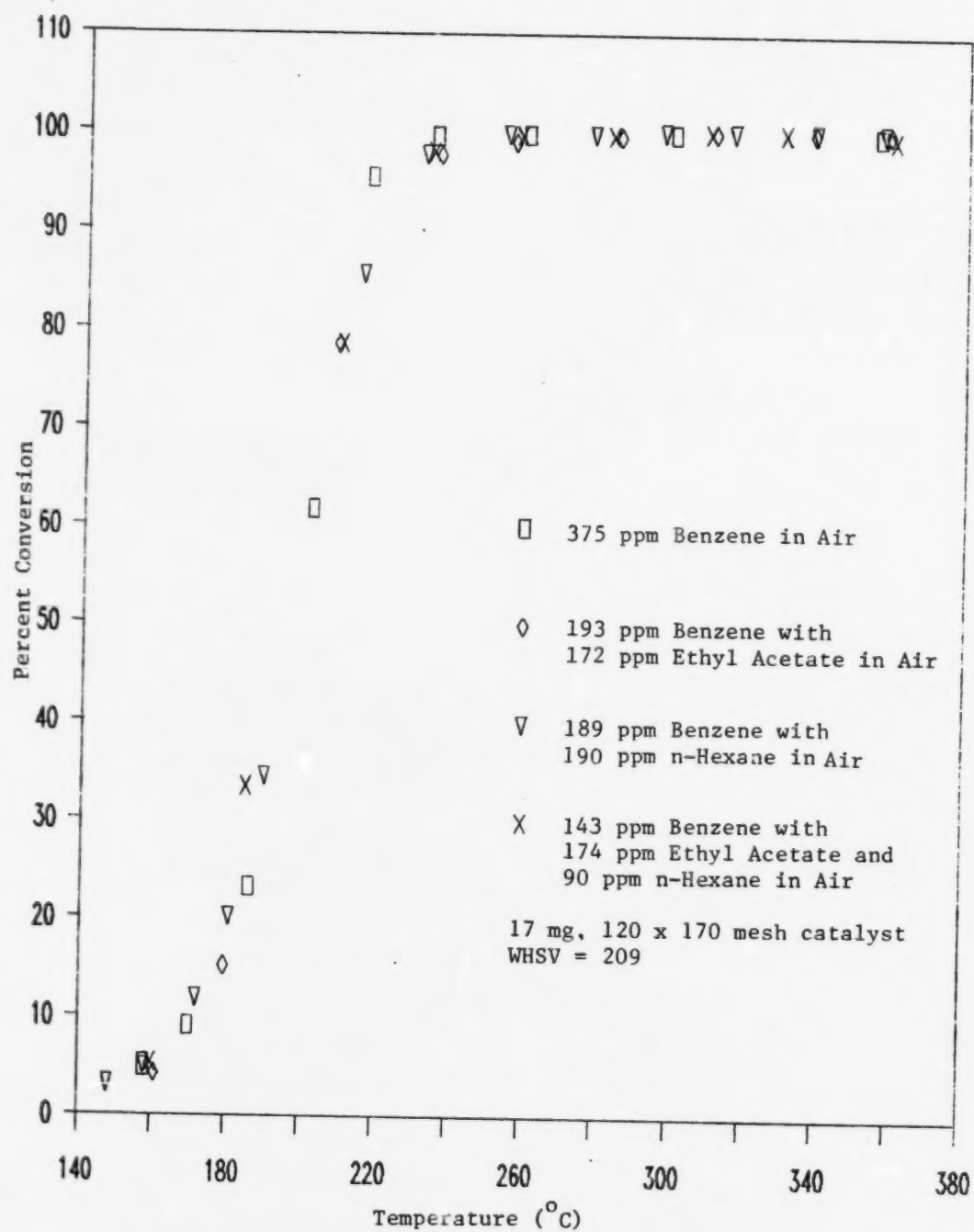


Figure 5. Effect of multicomponent mixtures on benzene conversion.

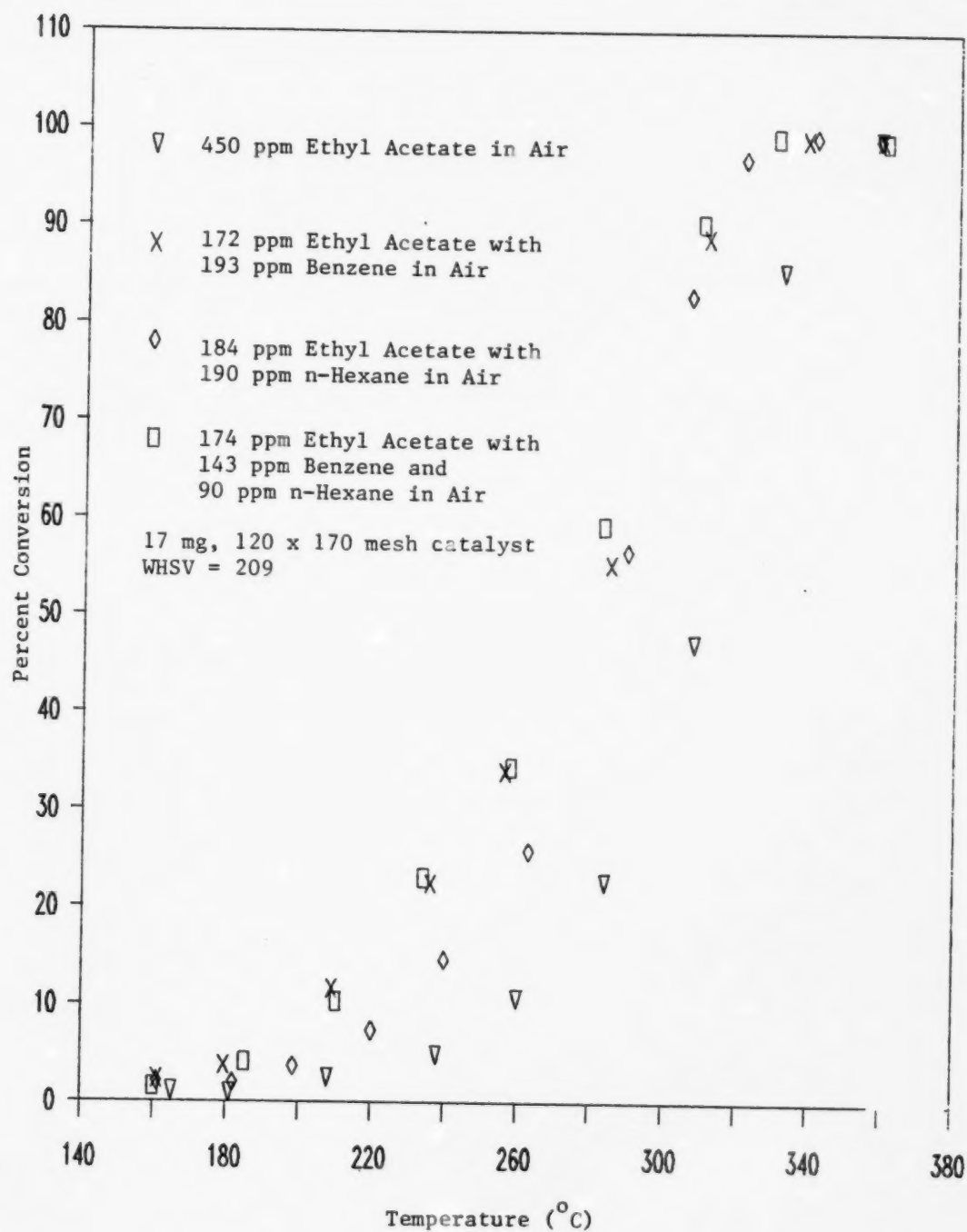


Figure 6. Effect of multicomponent mixtures on ethyl acetate conversion.

weight of catalyst per hour. A quick comparison of these figures with Figure 3 shows that the data have been obtained in regions A and B but not in C. The temperature range of 140 to 360 °C thus corresponds primarily to the intrinsic reaction and mass-transfer-controlled region. As corroboration of this, we may quote the results of Harrison and Ernst (1978) who show that catalytic combustion of carbon monoxide primarily occurs in regions A and B of Figure 3 at temperatures below 377 °C.

As shown in Figure 4, the conversion of n-hexane is significantly inhibited in mixtures versus as a single component. The inhibition at low temperatures (<260 °C) is highest in the presence of benzene. From Figure 5, the conversion of benzene appears to be nearly unaffected in the mixtures. Finally, from Figure 6, the conversion of ethyl acetate is significantly enhanced in the mixtures. This enhancement is highest in the mixtures containing benzene.

As pointed out earlier, all data in Figures 4 through 6 are at the same space velocity. Another way to present the data would be in terms of reaction-rate constants, which allows data at different space velocities to be represented concisely as shown in Equation (1). For deep oxidation of trace organics, the most popular assumption in the literature for kinetics is first order in terms of the organic concentration (Hawthorn 1974, Morooka et al. 1967, Sadamori et al. 1981, Prasad et al. 1984). Also, for oxidation of mixtures, it is usually assumed that each specie is oxidized independently (Prasad et al. 1984). (It is not implied here that the rate of oxidation of a specie in a mixture is identical to that as a single component.) Because all our experiments were carried out in large excesses of oxygen, a first-order kinetics assumption would enable us to determine a pseudo first-order rate constant for each oxidation reaction. With the further assumption of plug flow in the laboratory tubular reactor, a differential mass balance followed by integration yields the following equation for the pseudo first-order rate constant:

$$k_{ps} = \frac{(WHSV)}{3600 \rho_{GT}} \ln \left(\frac{C_{i0}}{C_i} \right) \quad (1)$$

k_{ps} may then be represented by the familiar Arrhenius equation

$$k_{ps} = A \exp [-E/RT] \quad (2)$$

It is emphasized here that Equation (1) should be regarded only as a way of representing the data because first-order kinetics may not apply. The advantages of Equations (1) and (2) are their simplicity and ability to represent a large amount of data concisely. It should also be noted that space velocity is incorporated into Equation (1), so that data at different space velocities may be represented. A further advantage is that the Arrhenius plot allows determination of temperature ranges for regions of surface-reaction control and mass-transfer control, as evident from Figure 7.

Figure 7 shows the first-order rate constants for the pure components. The order of reactivity of the three compounds is benzene > n-hexane > ethyl acetate. The inlet concentrations of the gases for these data were 525, 450, and 566 ppmv, respectively, for benzene, n-hexane, and ethyl acetate. The n-hexane plot exhibits the surface-reaction region below about 220 °C, because the rate constant appears to be nearly independent of catalyst particle size. Also, linearity of the plot in the surface-reaction region suggests that first-order kinetics may be a reasonable approximation for n-hexane oxidation. The Arrhenius plot for benzene also shows apparent first-order behavior at low temperatures, but the plot for ethyl acetate shows a distinct curvature indicating that first-order kinetics may not be a reasonable representation. The plot for benzene also appears to show a shift into the mass-transfer region at a temperature just below 220 °C, just as did n-hexane's plot.

Figure 7 for the single components is to be contrasted with the rate constants of the components in a ternary mixture (Figure 8). Ethyl acetate is now more reactive than n-hexane, and n-hexane's plot shows a curvature, indicating that first-order kinetics may not be obeyed in the mixture. Obviously, complex intercomponent interactions are present when mixtures are oxidized.

The apparent inhibitions and enhancements shown in Figures 4 through 8 may be caused by: (1) mixture effects involving competition for active sites and differences in external and internal mass-transfer rates, and

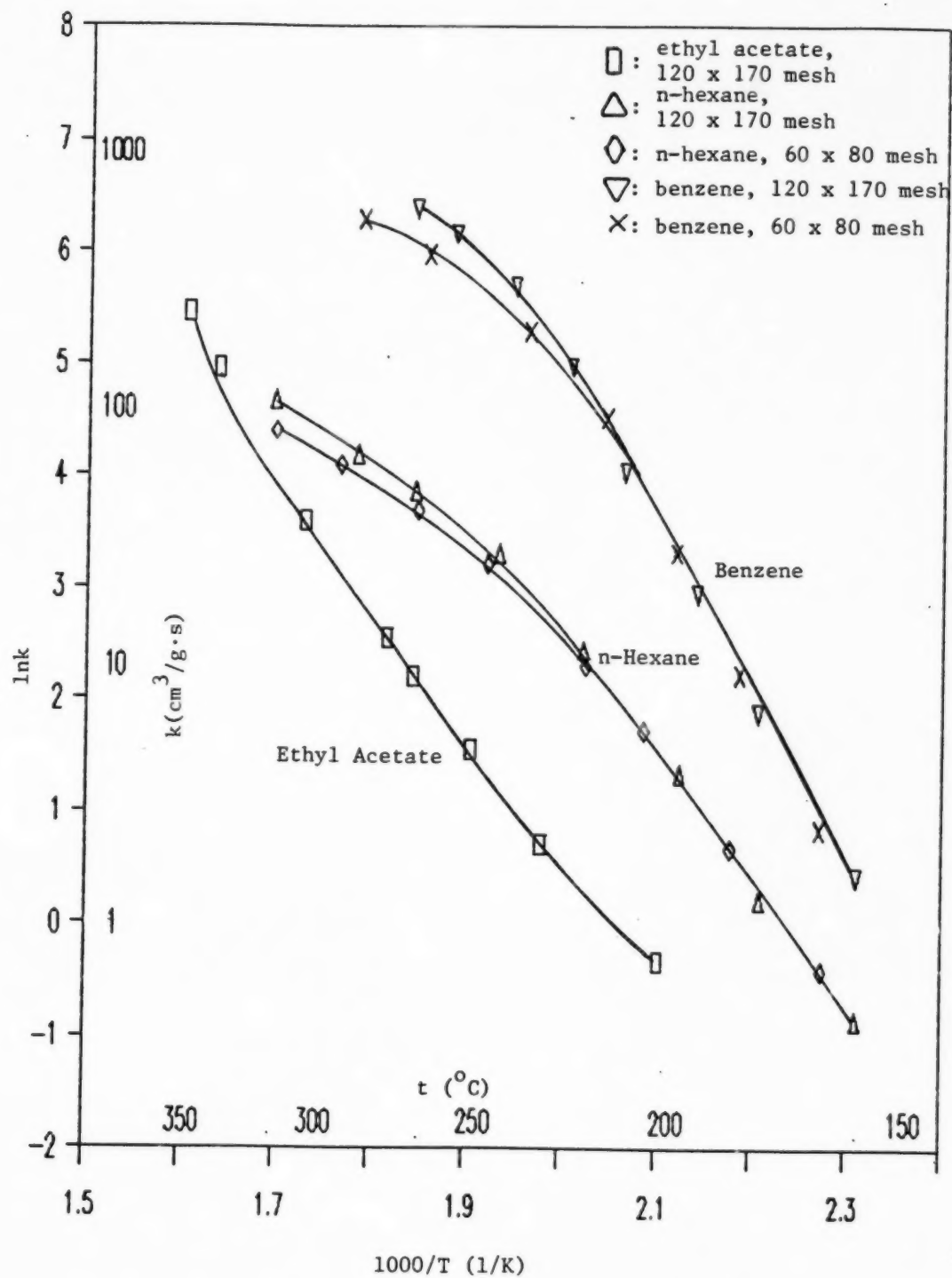


Figure 7. First-order rate constants for oxidation of single components.

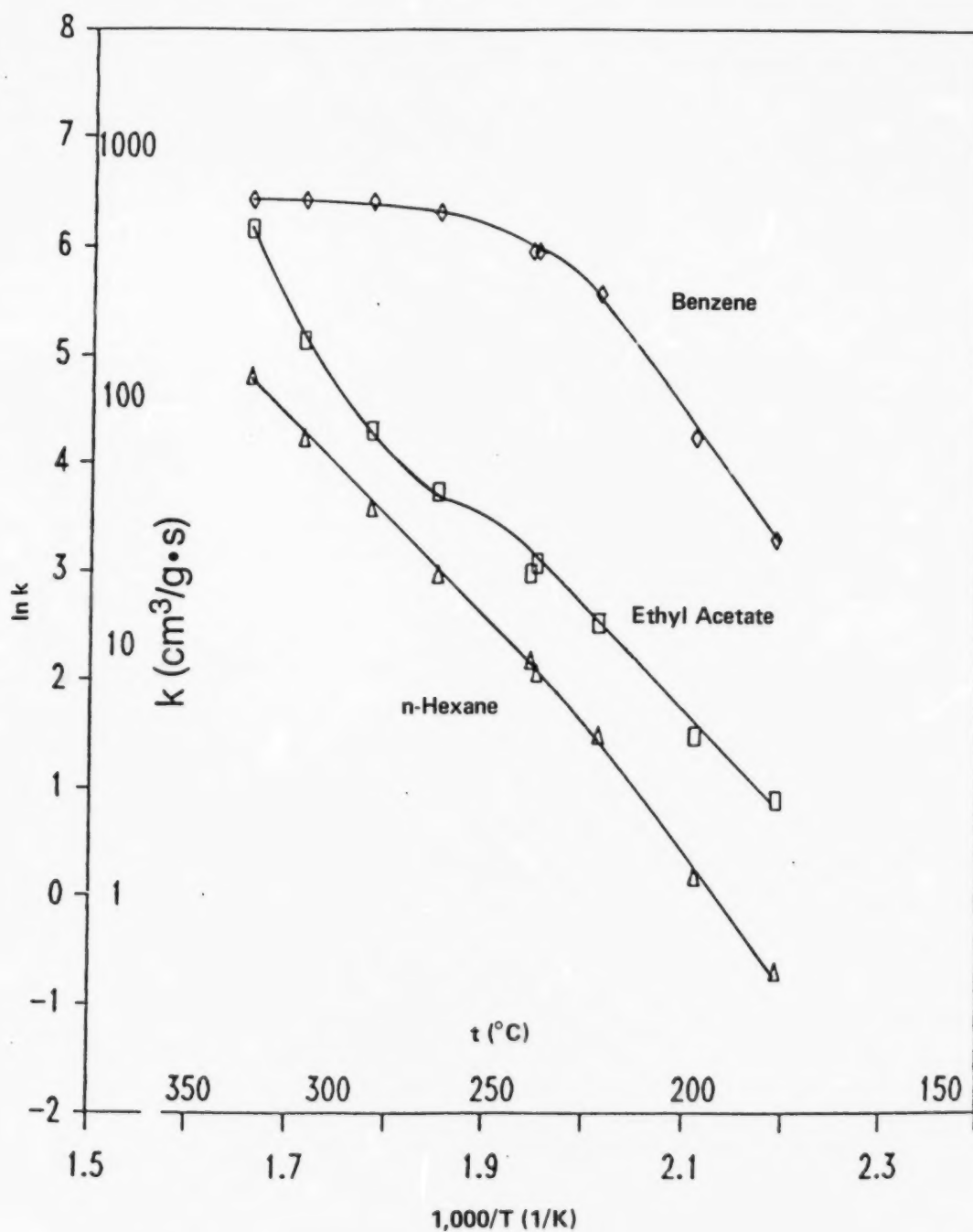


Figure 8. First-order rate constants for oxidation in a ternary mixture.

(2) mixture effects involving surface modification or cocatalysis by one of the reacting species. Of the reasons listed above, (1) appears to be mathematically tractable given that a suitable kinetic model for the reaction of the various species in a mixture may be developed. Once this is done, and the effects are still not explained, then a combination of (1) and (2) above or some other unknown complex interactions are probably involved. To sort this out, it was deemed necessary to obtain intrinsic kinetic rates for the three components individually. This was done by operating the reactor as a differential reactor (conversions between 5 and 8 percent) for the three components individually at a series of concentrations and temperatures. The temperatures chosen were generally below 220 °C (as guided by the previous experiments) to ensure that data were obtained in the surface kinetic region.

The rate data as a function of temperature and concentration are shown in Figures 9, 10, and 11 for n-hexane, benzene, and ethyl acetate, respectively. n-Hexane exhibits close to first-order behavior at temperatures up to 201 °C (Figure 9). On the other hand, benzene exhibits close to zero-order behavior at all temperatures tested, at concentrations above about 4×10^{-9} mol/cm³. Ethyl acetate has a reaction order between 0 and 1. We may fit an empirical power law kinetic expression to the differential data for n-hexane and ethyl acetate, and assume a zero-order behavior for benzene. Although these kinetic expressions would represent single-component behavior accurately in the intrinsic kinetic region, they would not be useful for explaining the complex interactions observed in the catalytic oxidation of mixtures. A more rigorous approach is to develop kinetic expressions involving surface interactions (e.g., Langmuir/Hinshelwood, Eley/Rideal, or Mars/van Krevlan) because they may allow explanation of the complex interactions; e.g., via competitive adsorption. This approach has been adopted and is detailed in the Discussion section of this paper.

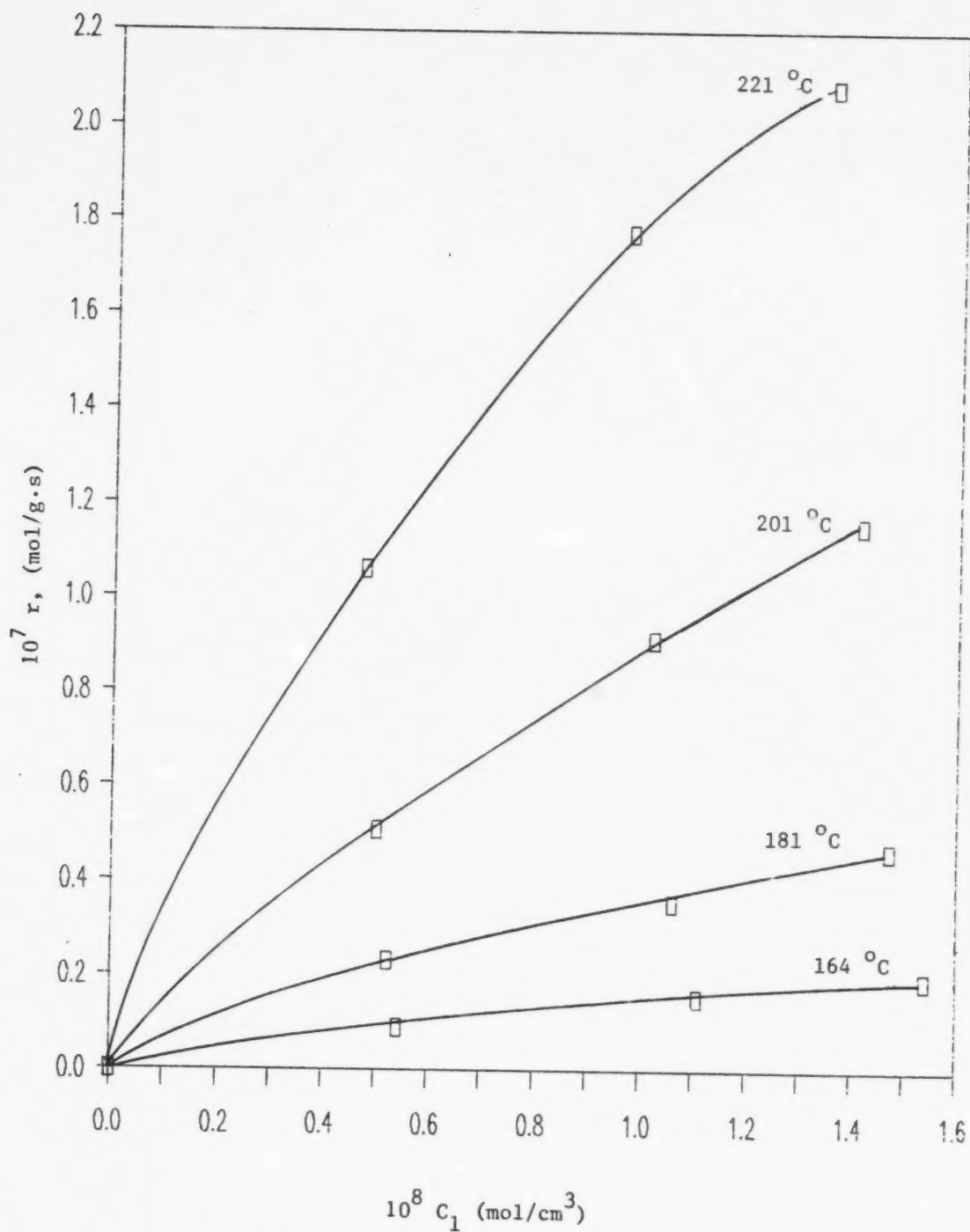


Figure 9. Differential reaction rate for n-hexane oxidation.

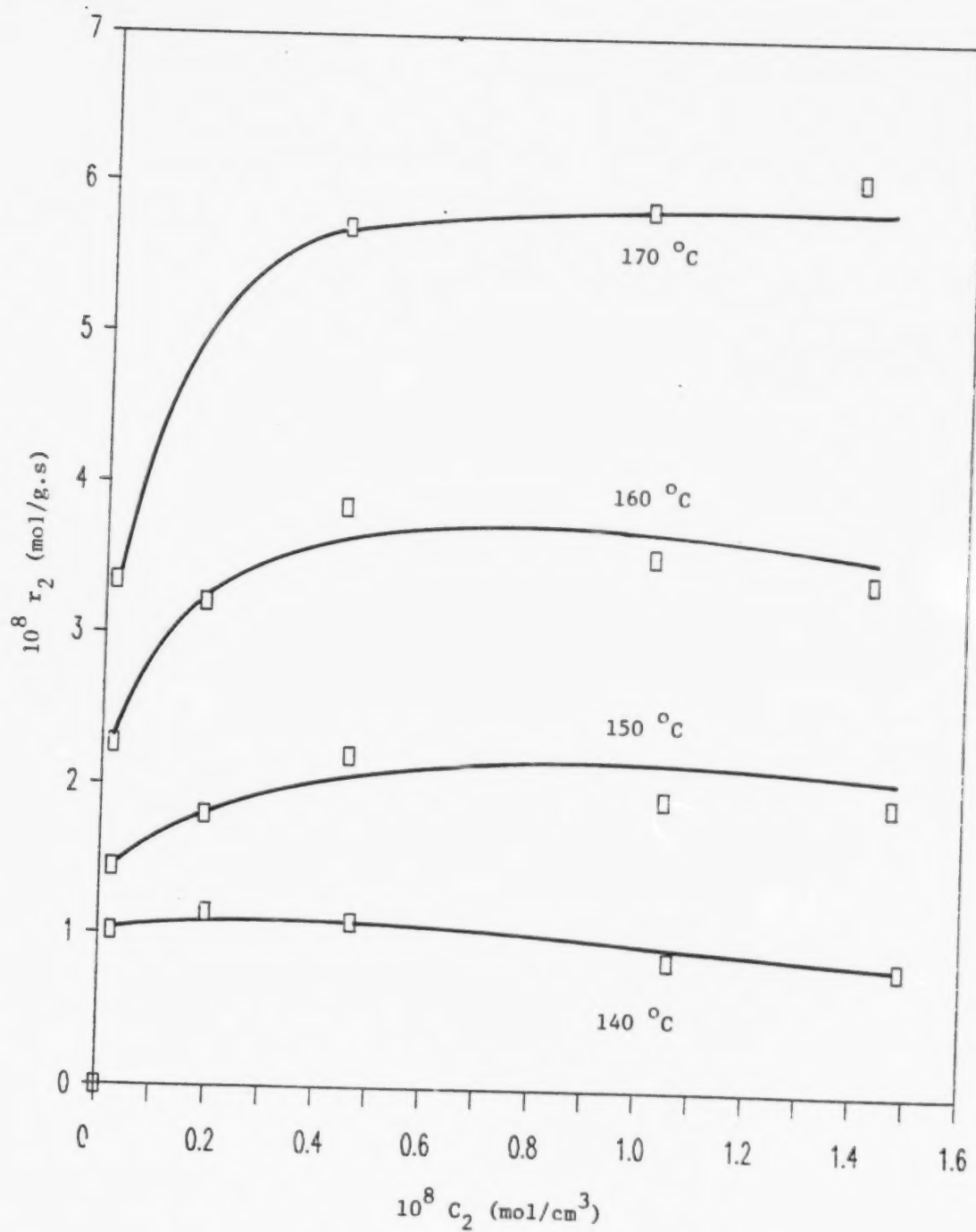


Figure 10. Differential reaction rate for benzene oxidation.

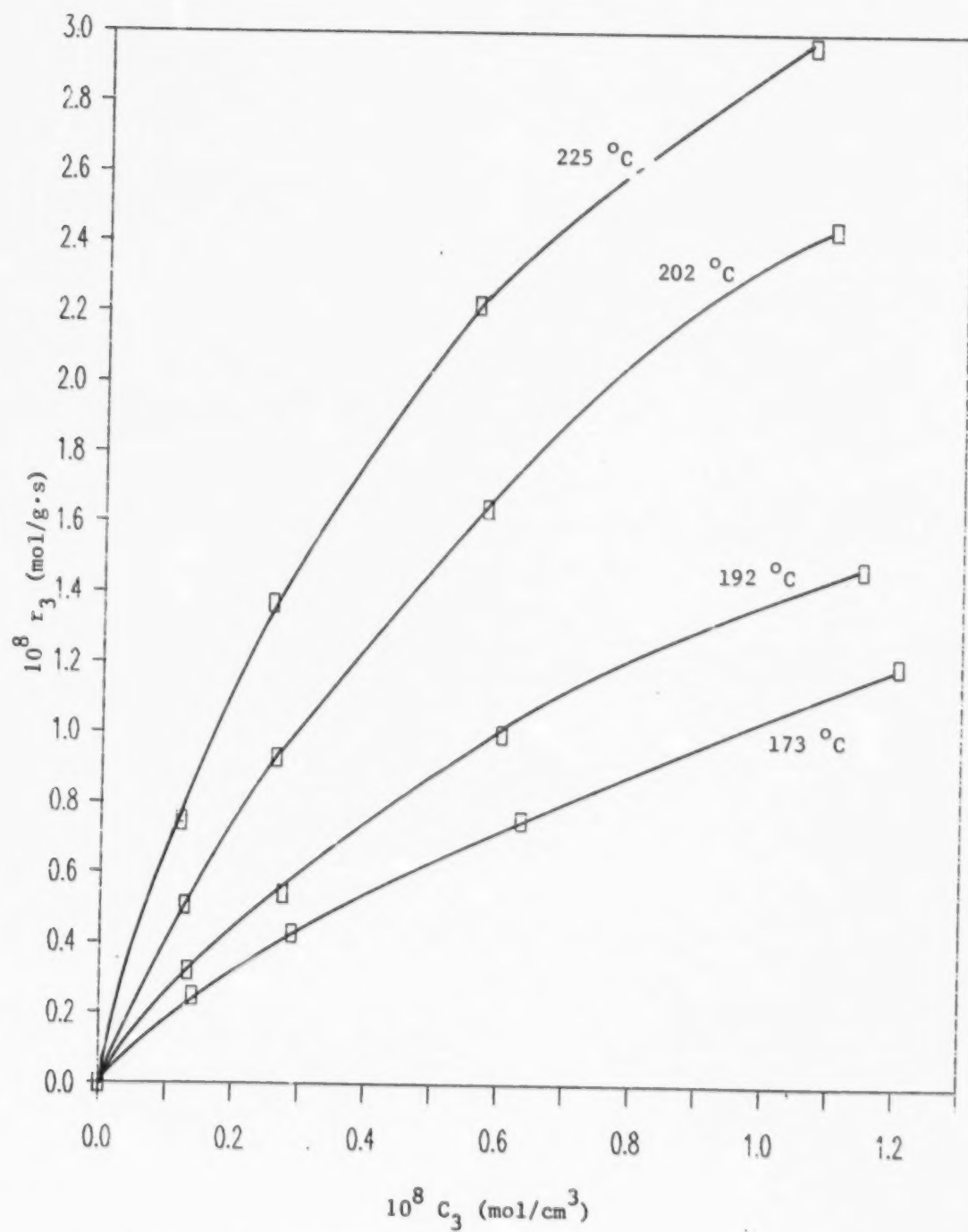
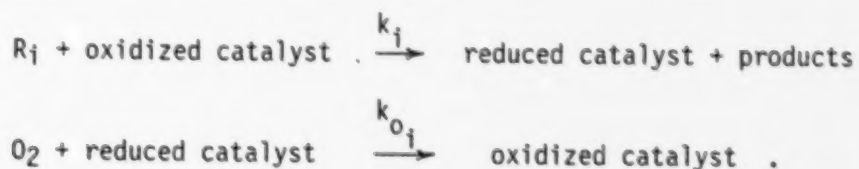


Figure 11. Differential reaction rate for ethyl acetate oxidation.

DISCUSSION

Mechanistic kinetic expressions are needed to represent the rate data obtained in Figures 9 through 11 and to quantitatively explain the complex effects observed in Figures 4 through 8. The mechanistic kinetic model that has received the widest support (Balasubramanian and Vishwanath 1975, Golodets 1983, Jaswal et al. 1969) for oxidation of organic compounds is due to Mars and van Krevlan (1954) and is:



In this mechanism, the above steps are assumed to be first order in the respective gaseous species. Thus, if θ is the fraction of oxidized catalyst at any time, then:

$$r_i = k_i C_i \theta \quad (3)$$

and

$$r_{O_2} = k_{o_i} C_O (1-\theta) \quad (4)$$

If stoichiometry for oxidation requires γ_i moles of oxygen per mole of hydrocarbon, then:

$$r_{O_2} = \gamma_i r_i \quad (5)$$

from Equations (3), (4), and (5), eliminating θ ,

$$r_i = \frac{k_{o_i} k_i C_O C_i}{k_{o_i} C_O + \gamma_i k_i C_i} \quad (6)$$

which is the Mars and van Krevlan rate expression for oxidation of hydrocarbon specie i . Note that the apparent experimentally observed order of the hydrocarbon oxidation rate with respect to the hydrocarbon specie varies between the extremes of 0 and 1. When:

$$k_{o_i} C_o \gg \gamma_i k_i C_i$$

then $r_i \approx k_i C_i$ (first order with respect to hydrocarbon), (7)

and when

$$k_{o_i} C_o \ll \gamma_i k_i C_i$$

then $r_i \approx \frac{k_o C_o}{\gamma_i}$ (zero order with respect to hydrocarbon). (8)

The next step is to evaluate the respective k values for the components of interest, namely, n-hexane, benzene, and ethyl acetate. This may be facilitated by inverting Equation (6):

$$\frac{1}{r_i} = \frac{1}{k_i} \cdot \frac{1}{C_i} + \frac{\gamma_i}{k_{o_i} C_o} \quad (9)$$

Because in our experiments C_o is nearly a constant due to the large excess of oxygen, Equation (9) should be a nearly linear relationship between inverse reaction rate and inverse concentration if Equation (6) adequately represents the oxidation rate data. Plots for $\frac{1}{r_i}$ vs. $\frac{1}{C_i}$ for n-hexane and ethyl acetate are shown in Figures 12 and 13, respectively, for several temperatures. The linearity of these plots lends credence to the Mars/van Krevlan mechanism for these species. Arrhenius relationships and plots for the corresponding k values are shown in Figures 14 and 15.

A problem is encountered if a similar approach for benzene is attempted because benzene exhibits nearly a zero-order behavior at concentrations greater than $4 \cdot 10^{-9}$ mol/cm³ (Figure 10). The limiting zero-order relationship is given by Equation (8), which may be used to evaluate k_{o_i} for benzene as a function of temperature from rate data in the nearly horizontal portions of the plots in Figure 10. k_i for benzene may be evaluated using the data at the lowest concentration from the limiting first-order Equation (7). Arrhenius plots for k_i and k_{o_i} evaluated in this manner

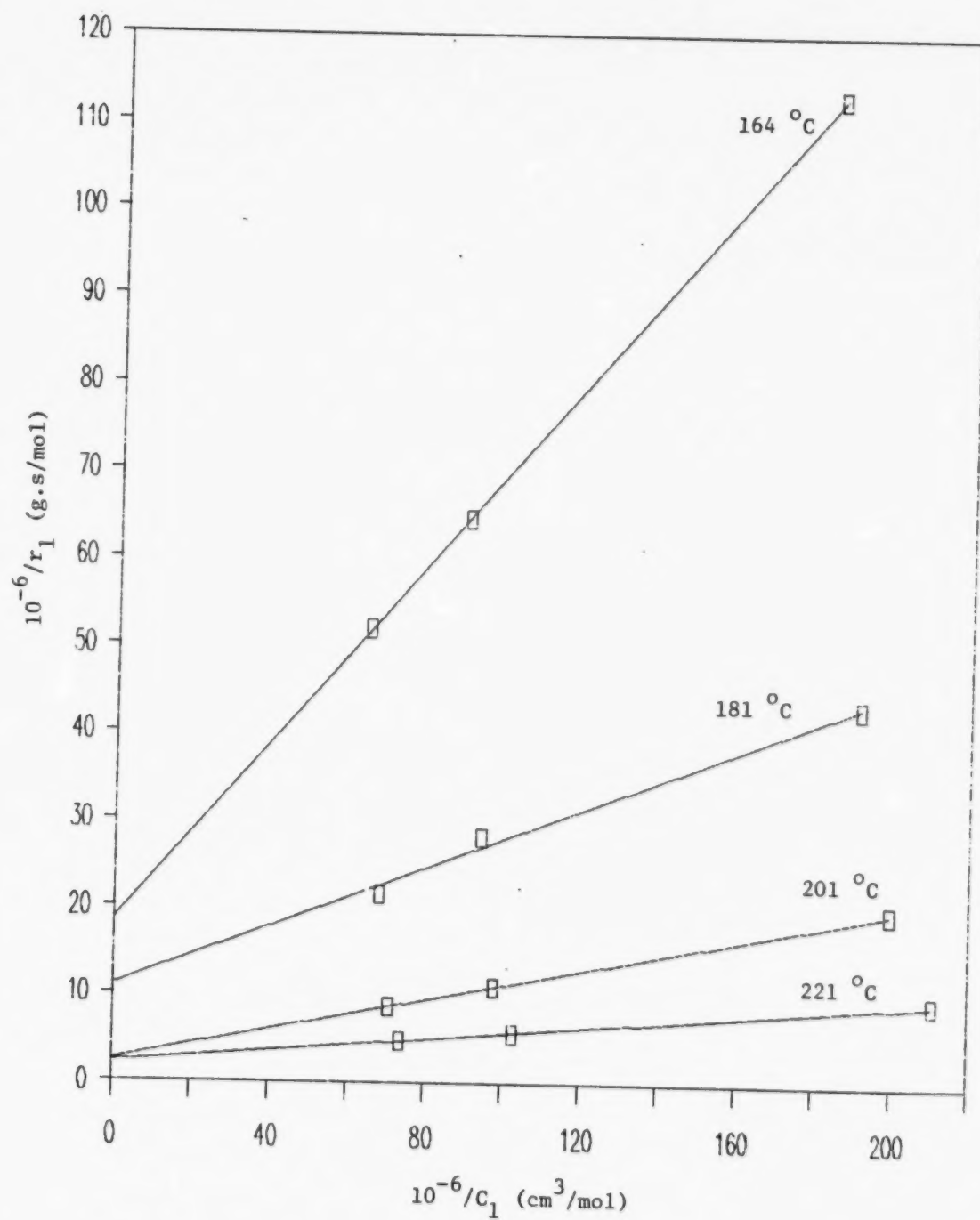


Figure 12. Inverse reaction rate versus inverse concentration for n-hexane oxidation.

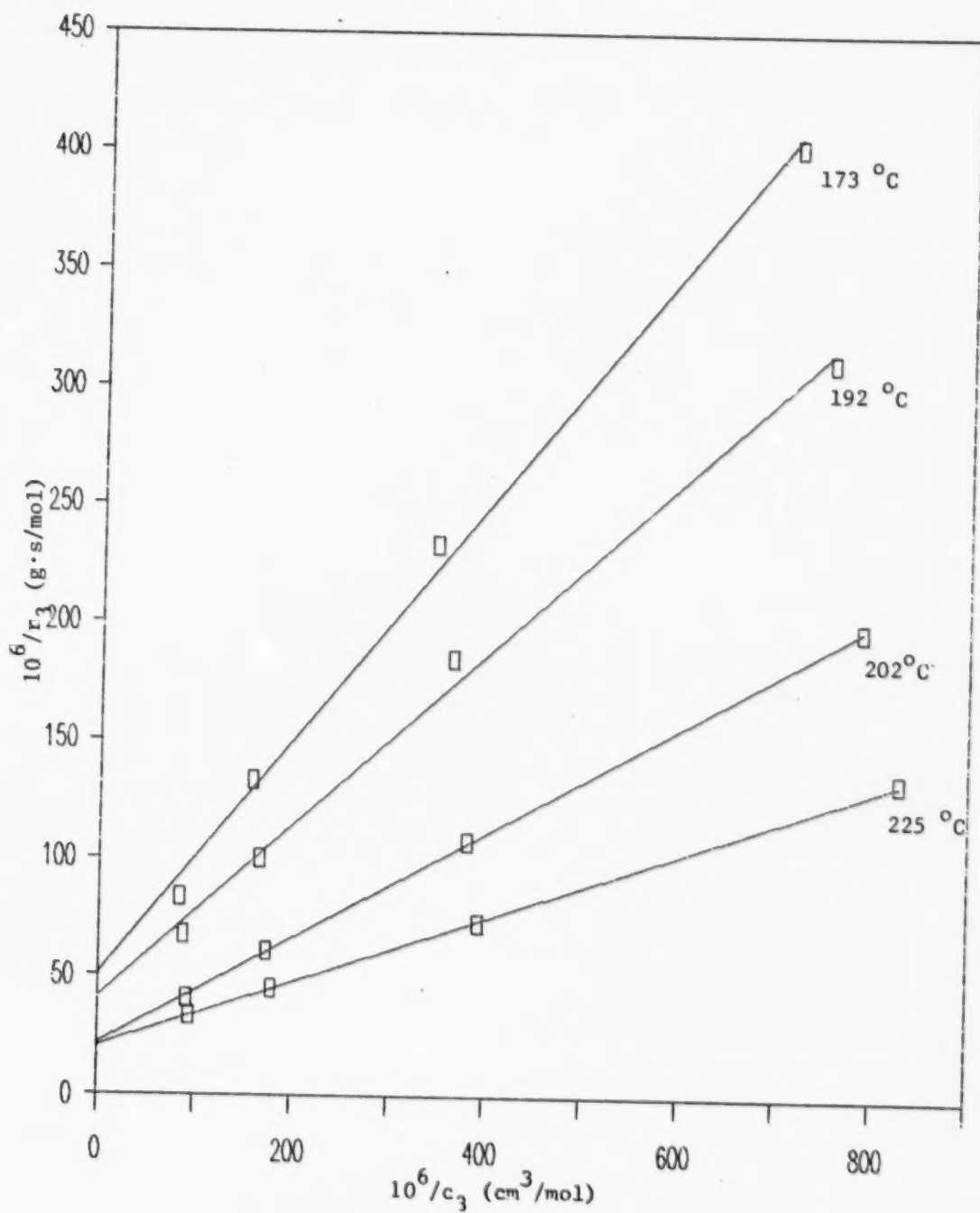


Figure 13. Inverse reaction rate versus inverse concentration for ethyl acetate oxidation.

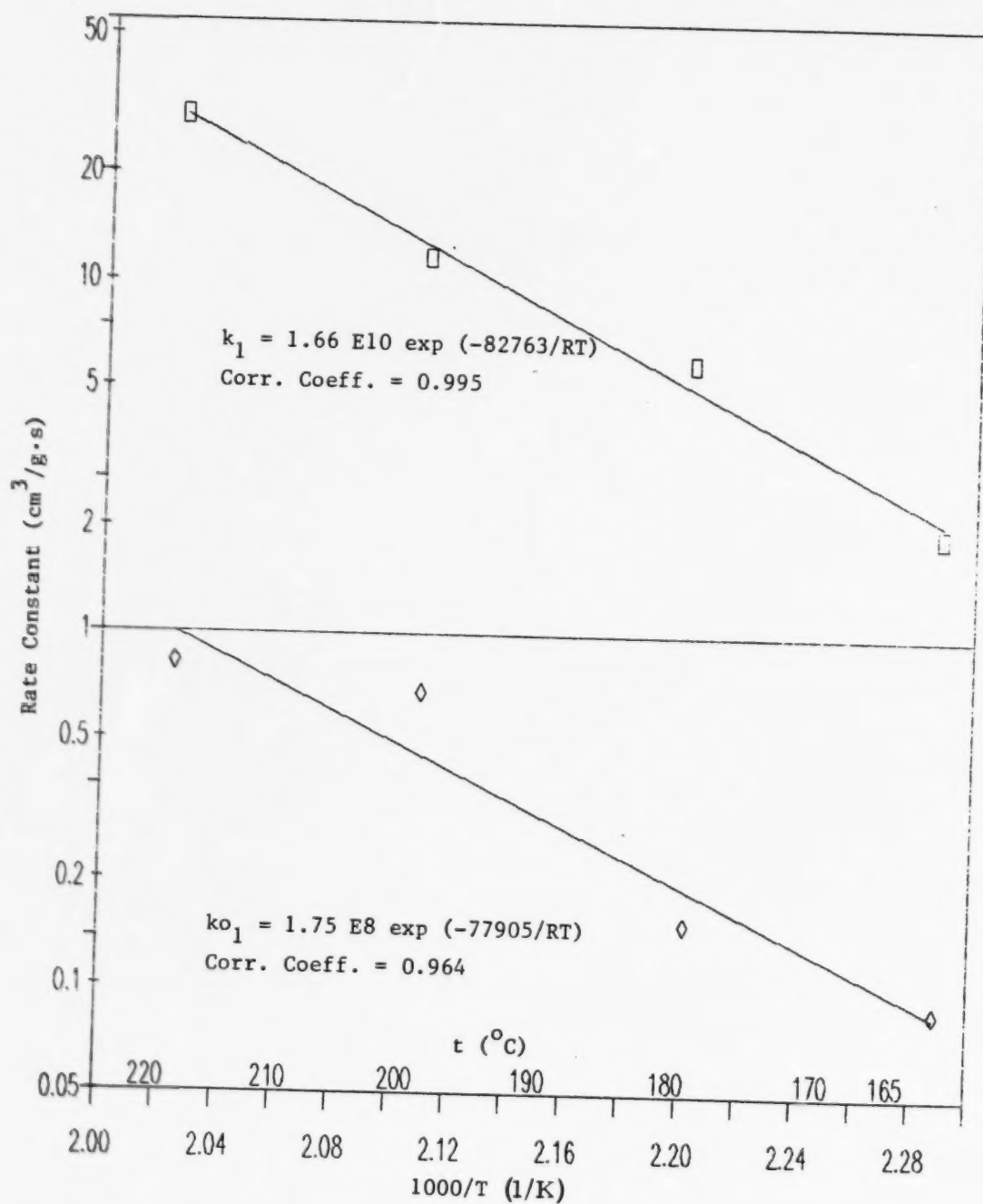


Figure 14. Mars/van Krevian rate constants for n-hexane oxidation.

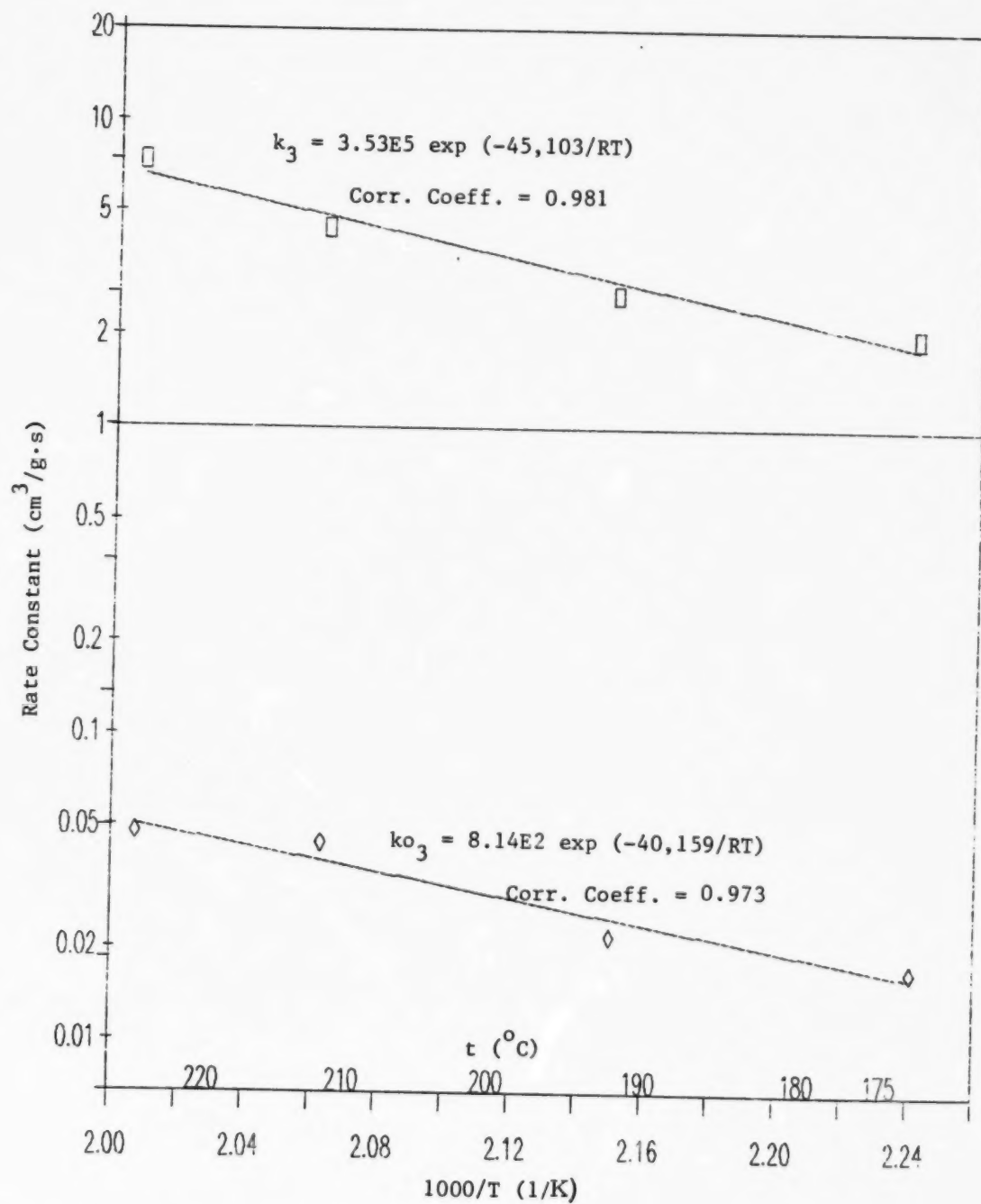
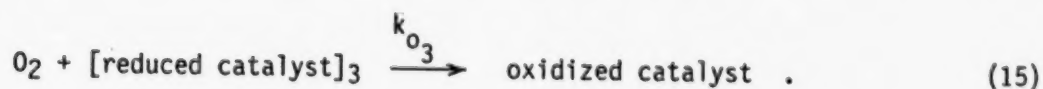
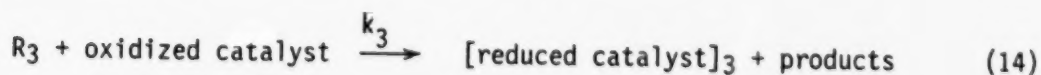
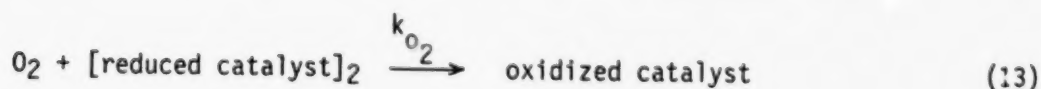
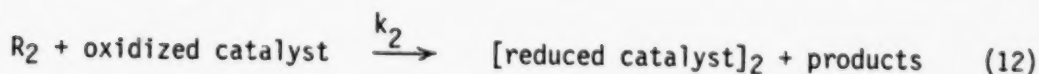
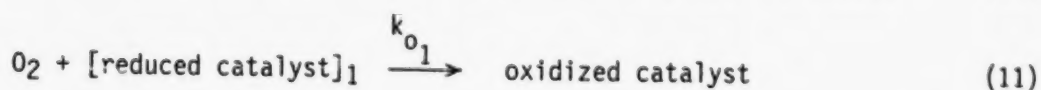
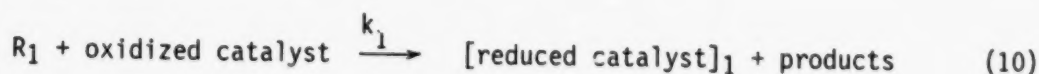


Figure 15. Mars/van Krevlan rate constants for ethyl acetate.

are shown in Figures 16 and 17, respectively. Only the three lowest temperatures have been used to evaluate k_i (Figure 16) because it was not possible to obtain the data at the highest temperature under true differential reactor conditions due to experimental limitations.

The complete Mars/van Krevlan formulations for the three components for oxidation as single components are summarized in Table 4. To apply these relationships to the complex mixture effects shown in Figures 4 to 6, a multicomponent model needs to be postulated based on the Mars/van Krevlan mechanism.

Because the reoxidation rate constants (k_{o_i} 's) for the various hydrocarbons are different, it is reasonable to assume that the catalytic species is reduced to different oxidation states by the different hydrocarbons. n-Hexane, benzene, and ethyl acetate as R_1 , R_2 , and R_3 , respectively, are designated. Then, for oxidation of a mixture of these hydrocarbons, the following may be postulated:



If at any instant θ_1 , θ_2 , θ_3 are the fractions of the catalyst surface occupied by $[\text{reduced catalyst}]_1$, $[\text{reduced catalyst}]_2$, and $[\text{reduced catalyst}]_3$, respectively, then the following balances may be written:

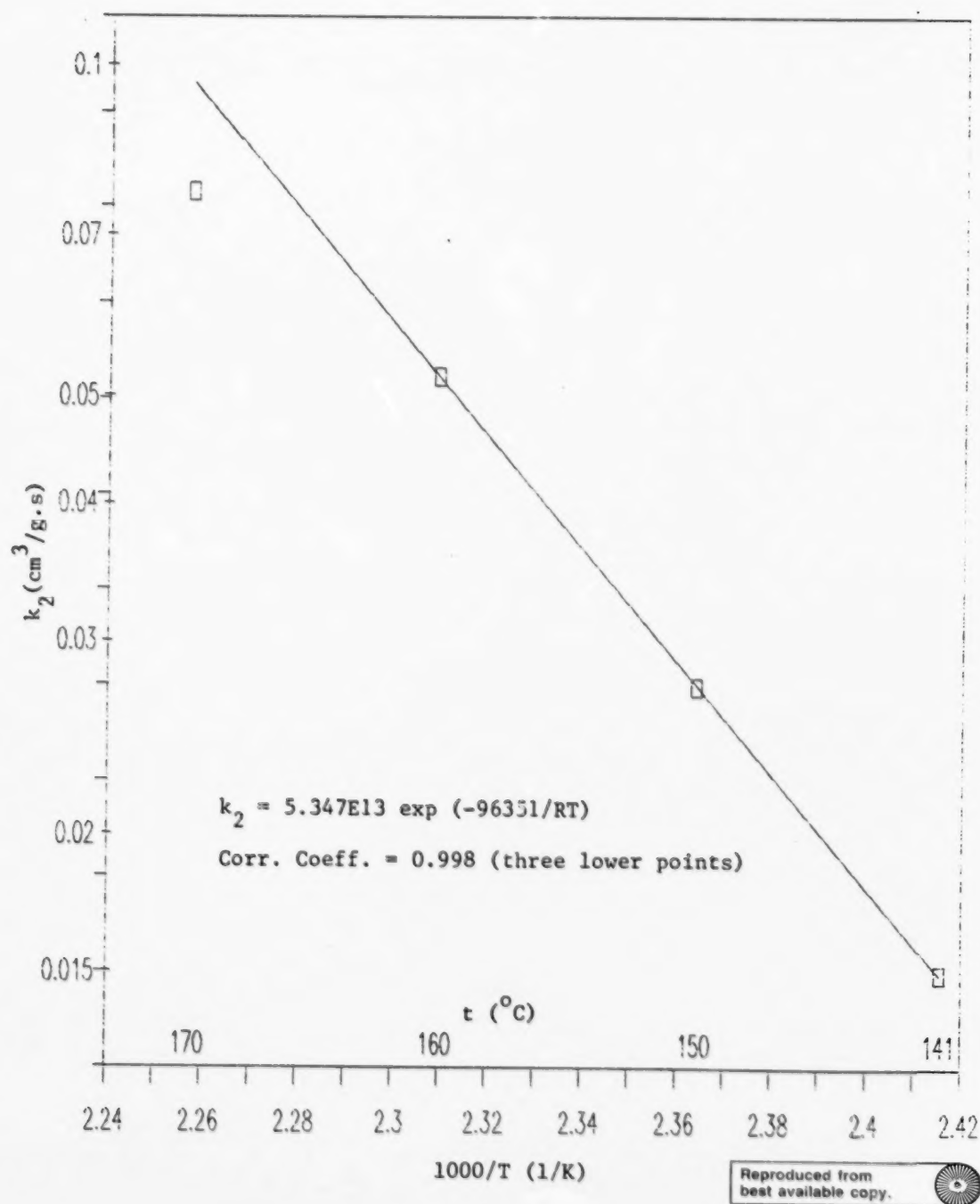


Figure 16. Mars/van Krevlan surface-reduction rate constant for benzene.

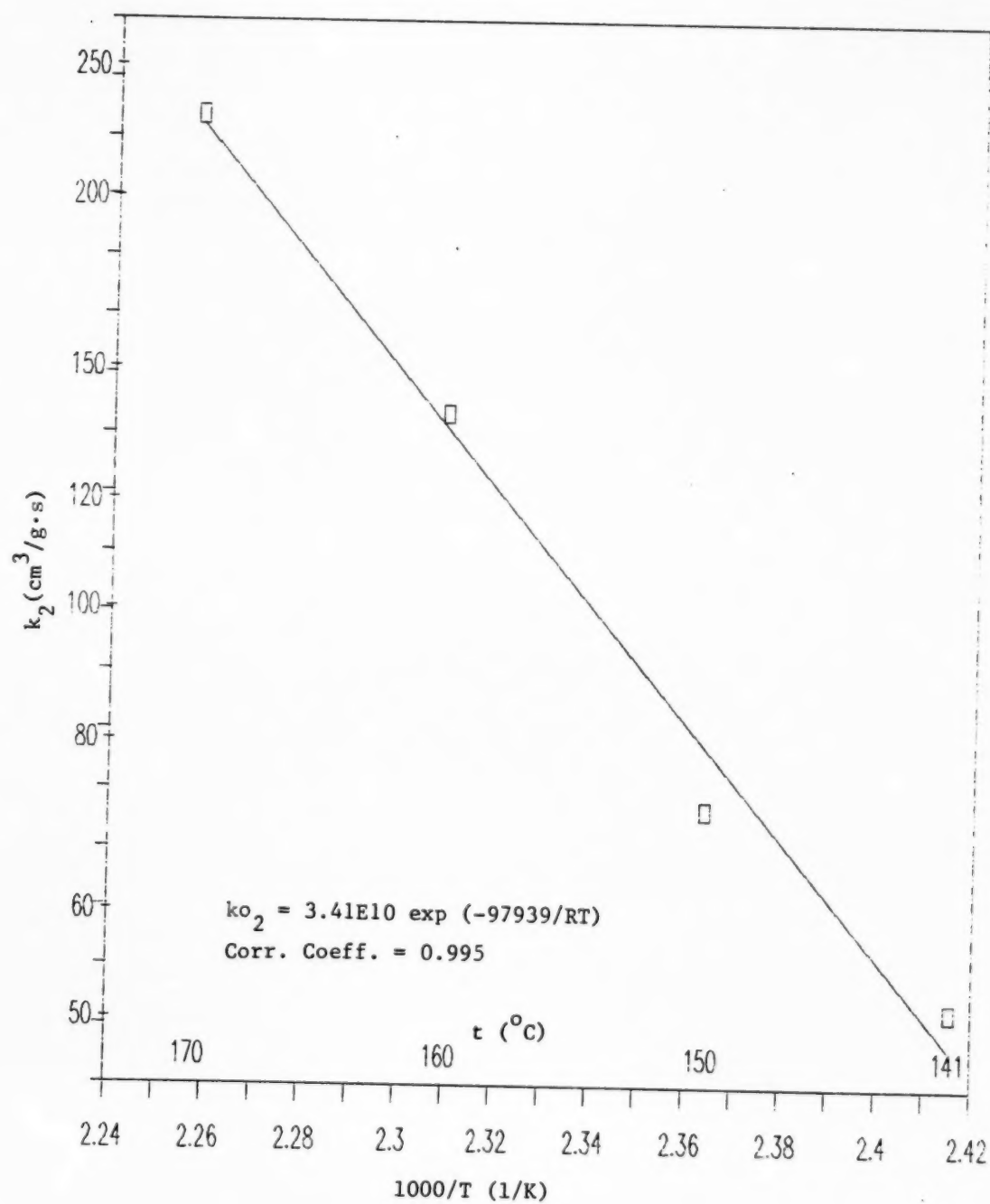


Figure 17. Mars/van Krevlan surface-reoxidation rate constant for benzene.

TABLE 4. MARS/VAN KREVLAN RATE EQUATION PARAMETERS

$$r_i = \frac{k_{o_i} k_i C_o C_i}{k_{o_i} C_o + \gamma_i k_i C_i}$$

	$k_{o_i}, \left(\frac{\text{cm}^3}{\text{g}\cdot\text{s}}\right)$	$k_i, \left(\frac{\text{cm}^3}{\text{g}\cdot\text{s}}\right)$	γ_i (--)
n-hexane	$1.75 \cdot 10^8 \exp [-77,905/\text{RT}]$	$1.66 \cdot 10^{10} \exp [-82,763/\text{RT}]$	9.5
benzene	$3.41 \cdot 10^{10} \exp [-97,939/\text{RT}]$	$5.347 \cdot 10^{13} \exp [-96,351/\text{RT}]$	7.5
ethyl acetate	$8.14 \cdot 10^2 \exp [-40,159/\text{RT}]$	$3.533 \cdot 10^4 \exp [-45,108/\text{RT}]$	5

$$r_1 = k_1 C_1 (1-\theta_1-\theta_2-\theta_3) = \gamma_1 k_{o1} C_o \theta_1 \quad (16)$$

$$r_2 = k_2 C_2 (1-\theta_1-\theta_2-\theta_3) = \gamma_2 k_{o2} C_o \theta_2 \quad (17)$$

$$r_3 = k_3 C_3 (1-\theta_1-\theta_2-\theta_3) = \gamma_3 k_{o3} C_o \theta_3 \quad (18)$$

θ_1 , θ_2 , and θ_3 may be evaluated from Equations (16), (17), and (18) and substituted in the right-hand sides of these equations to yield the respective rate equations for oxidation in a multicomponent mixture:

$$r_1 = \frac{k_{o1} k_1 C_o C_1}{k_{o1} C_o + \gamma_1 k_1 C_1 + \gamma_2 \left[\frac{k_{o1}}{k_{o2}} \right] k_2 C_2 + \gamma_3 \left[\frac{k_{o1}}{k_{o3}} \right] k_3 C_3} \quad (19)$$

$$r_2 = \frac{k_{o2} k_2 C_o C_2}{k_{o2} C_o + \gamma_2 k_2 C_2 + \gamma_1 \left[\frac{k_{o2}}{k_{o1}} \right] k_1 C_1 + \gamma_3 \left[\frac{k_{o2}}{k_{o3}} \right] k_3 C_3} \quad (20)$$

$$r_3 = \frac{k_{o3} k_3 C_o C_3}{k_{o3} C_o + \gamma_3 k_3 C_3 + \gamma_1 \left[\frac{k_{o3}}{k_{o1}} \right] k_1 C_1 + \gamma_2 \left[\frac{k_{o3}}{k_{o2}} \right] k_2 C_2} \quad (21)$$

A general rate form for deep oxidation of the i th component in an n -component mixture may be easily inferred from Equations (19) to (21):

$$r_i = \frac{k_{o_i} k_i C_o C_i}{k_{o_i} C_o + \sum_{j=1}^n \frac{k_{o_i}}{k_{o_j}} \gamma_j k_j C_j}, \quad i = 1, 2, \dots, n \quad (22)$$

Using single-component rate data (Table 4), Equation (22) may be used to predict the conversion of each hydrocarbon component in a mixture, in the intrinsic kinetic region (i.e., lower portions of Figures 4 through 6 corresponding to region A of Figure 3). If such a multicomponent model is credible, then the predicted conversions should be close to the experimentally observed conversions. The model predictions would require setting up component balances for each specie. Because a tubular reactor has been used in our experiments, the rate of reaction changes along the bed because the concentrations change along the bed. Thus, differential component balances (assuming plug flow) have been set up as follows for an n-component mixture:

$$\frac{d f_i}{dw} = \frac{r_i}{v_o C_{i0}}, \quad i = 1, 2, \dots, n \quad (23)$$

$$\text{with inlet boundary condition, } f_i(0) = 0, i=1, 2, \dots, n \quad (24)$$

where f_i is the fractional conversion of specie i and w is the catalyst weight.

The n-coupled ordinary nonlinear first-order differential equations for an n-component mixture must be solved simultaneously using a suitable numerical technique. A fourth-order Runge-Kutta method has been used to solve these equations and to evaluate conversions of the various VOCs in binary and ternary mixtures. Only the results for the binary mixtures of n-hexane and benzene, and n-hexane and ethyl acetate are presented because similar results were obtained for other mixtures. The model evaluations for the two binary mixtures (n-hexane/benzene and n-hexane/ethyl acetate) are compared to the actual experimental results (from Figures 4 through 6) in Figures 18 and 19, respectively.

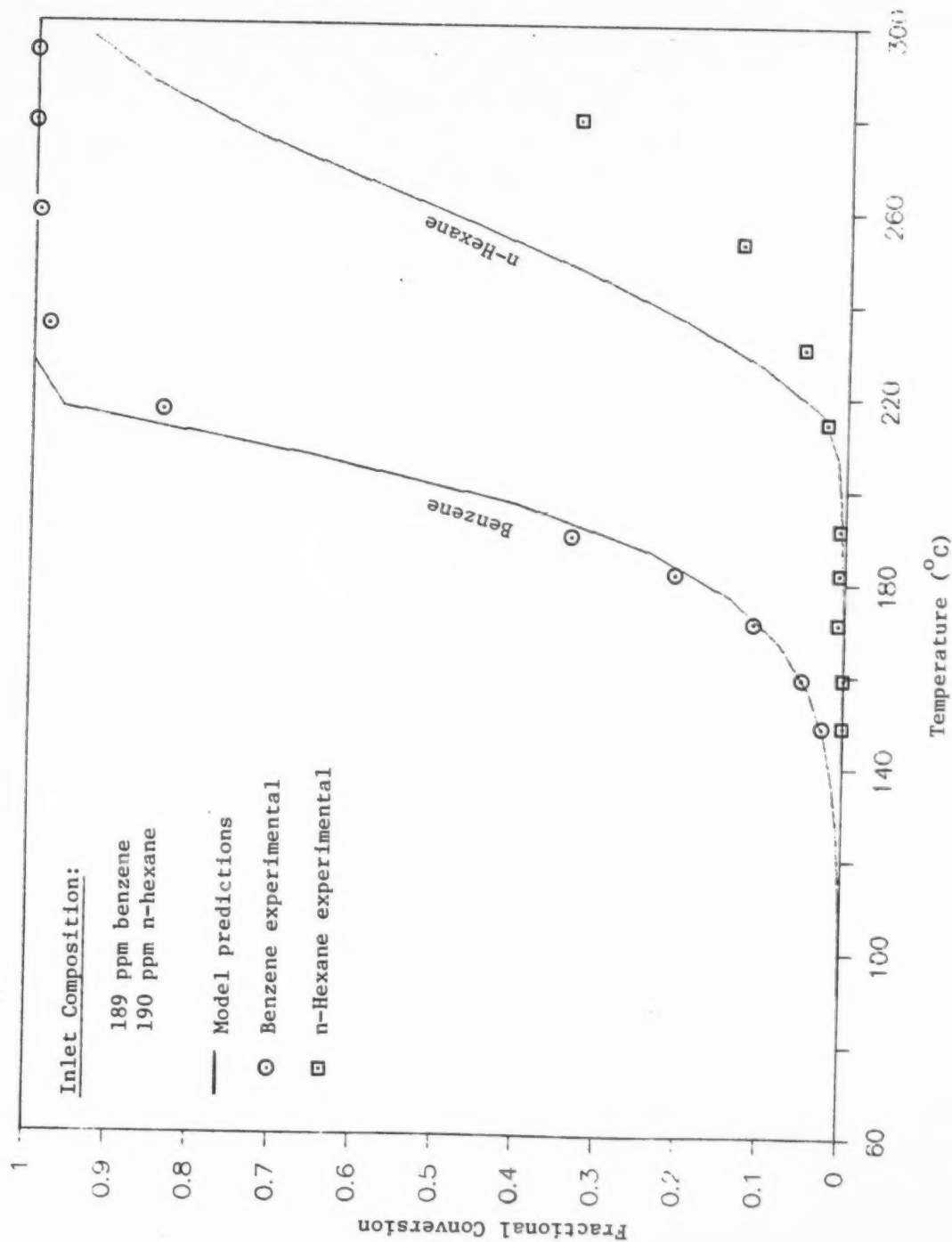


Figure 18. Comparison of predicted and actual conversions for benzene and n-hexane in a binary mixture.

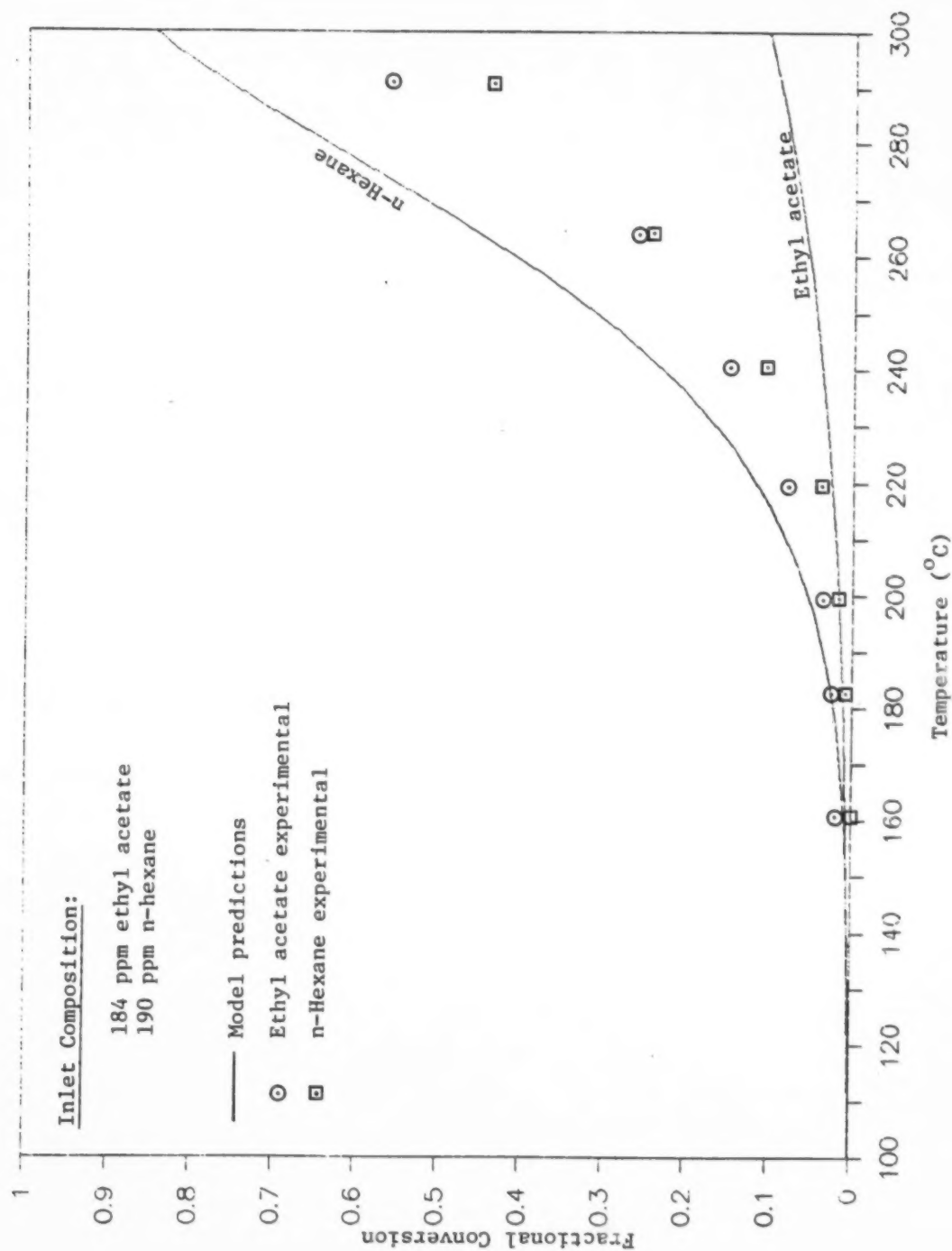


Figure 19. Comparison of predicted and actual conversions for ethyl acetate and n-hexane in a binary mixture.

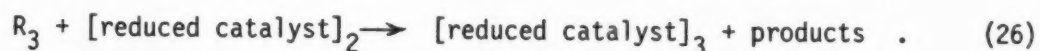
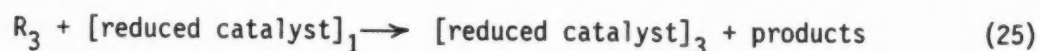
Considering Figure 18 first, the model predicts the experimentally observed conversions of benzene and n-hexane quite well up to approximately 220 °C. This corresponds nearly exactly to the onset of the mass-transfer region as seen in Figure 7. Above 220 °C, as expected, the model begins to overpredict the experimentally observed conversions, because the inhibiting effect of pore diffusion/external diffusion have not been incorporated into the model. RTI is currently attempting to refine the proposed model to incorporate these mass-transfer effects. This may be achieved by evaluating global rates of reaction for each VOC and substituting them in place of the intrinsic rate of reaction, r_i , in Equation (23). Evaluation of the global rates of individual species in a multicomponent mixture is by no means a simple task. For example, an attempt to incorporate only the pore-diffusion effect (let alone both pore diffusion and external diffusion) would require simultaneous solution of intraparticle differential mass-balance equations for the various hydrocarbon species.

Much more severe limitation of the proposed model is seen in Figure 19. The model overpredicts n-hexane conversion and underpredicts ethyl acetate conversion nearly throughout the temperature range shown. The overprediction of n-hexane in Figure 19 at temperatures below 220 °C indicates complex effects in the intrinsic kinetic region, associated with the presence of an oxygenated specie (i.e., ethyl acetate) as opposed to a nonoxygenated specie (i.e., benzene in Figure 18). Even more intriguing is the enhancement of ethyl acetate oxidation in mixtures (Figure 6). The proposed model cannot possibly predict enhancement (i.e., it can only predict inhibition) because of an increase in the value of the denominator of the rate equation (Equation [22] in a multicomponent mixture versus Equation [6] for a single component). Thus, a more rigorous model is necessary for mixtures containing ethyl acetate.

Predictions using the proposed model for other mixtures containing ethyl acetate are not shown herein but were similar. For example, for the benzene/ethyl-acetate mixture, the model overpredicted benzene conversion and severely underpredicted ethyl acetate conversion throughout the temperature range. For the ternary benzene/ethyl-acetate/n-hexane mixture, the model overpredicted the conversions of benzene and n-hexane and severely

underpredicted the conversion of ethyl acetate throughout the temperature range.

The complete breakdown of the model in the presence of ethyl acetate suggests that the partially oxygenated structure of ethyl acetate may play a strong role in multicomponent oxidation kinetics. A more rigorous multicomponent kinetic model is needed. Assuming the Mars/van Krevlan mechanism to apply, a logical extension of the proposed model (Equations [10] to [15]) would be to include the interaction of ethyl acetate with catalyst species reduced by the more strongly reducing species, namely benzene and n-hexane:



The model composed of Equations (10) to (15), (25), and (26) would yield a different set of intrinsic rate equations, but rate constants for Equations (25) and (26) must be obtained experimentally before this new set of intrinsic rate equations may be used. It is to be noted that the addition of steps (25) and (26) to the proposed model would enable the prediction of enhancement for ethyl acetate if these are additional ethyl-acetate-consuming steps.

Summarizing the modeling work, the multicomponent kinetic model (Equations [10] to [15]) based on the Mars/van Krevlan mechanism was found to be adequate for predicting oxidation of non-oxygenated hydrocarbons such as benzene and n-hexane in the intrinsic kinetic region. This model may be extended into the mass-transfer region by using global rates of reaction in place of the intrinsic rates of reaction in Equation (23). The simple model (Equations [10] to [15]) broke down when ethyl acetate was present in the VOC mixture to be oxidized. A more rigorous kinetic model is needed to predict multicomponent oxidations when partially oxygenated species such as ethyl acetate are present.

CONCLUSIONS

Based on the work to date, we may draw the following conclusions:

1. Deep catalytic oxidation rates of components in a mixture of VOCs may be substantially higher or lower than when present by themselves.
2. Mars/van Krevlan mechanism appears to be an adequate representation for the deep oxidation of single VOCs.
3. A simple multicomponent kinetic model (Equations [10] to [15]) based on the Mars/van Krevlan mechanism appears to be adequate in the intrinsic kinetic region when no oxygenated VOCs such as ethyl acetate are present in the reaction mixture.
4. Extension of the kinetic model (Equation [10] to [15]) to the mass-transfer region would require evaluation of global rates of reaction by simultaneously solving multiple intraparticle differential mass-balance equations.
5. Oxidation rates of oxygenated VOCs such as ethyl acetate are higher in VOC mixtures than as single components. A kinetic model to account for this enhancement will require incorporating second-order interactions between the components (e.g., Equations [25] and [26]).

NOMENCLATURE

	Units
A = preexponential factor	[cm ³ /(g•s)]
C _i = hydrocarbon [VOC] concentration	[mol/cm ³]
C _{io} = inlet hydrocarbon [VOC] concentration	[mol/cm ³]
C _O = oxygen concentration	[mol/cm ³]
E = activation energy	[J/mol.K]
f _i = fractional conversion of specie i	(--)
k _i = surface reduction rate constant for specie i	[cm ³ /(g•s)]
k _{o_i} = surface reoxidation rate constant for specie i	[cm ³ /(g•s)]
k _{ps} = pseudo first-order rate constant	[cm ³ /(g•s)]
R = gas constant, 8.314	J/(mol.K)
R _i = hydrocarbon specie, i	[--]
r _i = rate of oxidation of specie i	[mol/(g•s)]
r _{o₂} = rate of oxygen consumption	[mol/(g•s)]
T = absolute temperature	[K]
t = temperature	[°C]
v _O = volumetric flow rate at reaction temperature	[cm ³ /s]
WHSV = weight hourly space velocity	[g gas/(g catalyst•h)]

Greek Symbols

γ _i = stoichiometric coefficient for deep oxidation of specie i	[--]
θ = fraction of oxidized catalyst	[--]
θ _{1,θ₂,θ₃} = fraction of reduced catalyst corresponding to n-hexane, benzene, and ethyl acetate, respectively	[--]
ρ _{GT} = density of reaction gas at reaction temperatures	(g/cm ³)

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